A STUDY OF
THE ABSORPTION SPECTRA

OF

SOLUTIONS OF CERTAIN SALTS OF POTASSIUM, COBALT, NICKEL, COPPER,
CHROMIUM, ERBIUM, PRASEODYMIUM, NEODYMIUM, AND
URANIUM AS AFFECTED BY CHEMICAL AGENTS
AND BY TEMPERATURE

BY

HARRY C. JONES AND W. W. STRONG

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PREFACE.

This investigation on the absorption spectra of solutions is a continuation of the work of Jones and Uhler and Jones and Anderson, and has been made possible by grants generously awarded by the Carnegie Institution of Washington. The results obtained from the study of about 3000 solutions are recorded in this monograph. These include salts of potassium with a colored anion, cobalt, nickel, copper, chromium, erbium, praseodymium, neodymium, and uranyl and uranous uranium.

The effect of the addition of free acids and foreign salts on the absorption spectra is studied at some length and in considerable detail, and results have been obtained which show that chemical reactions in general are probably much more complex than is represented by the equations which are usually employed to express such chemical changes.

The effect of the nature of the solvents on the absorption spectra of substances dissolved in those solvents has been one of the chief points investigated in this work. It is shown that solvents which themselves do not absorb visible light may have a determining influence on the absorption of the dissolved substances. Well-defined "solvent-bands" have been discovered for water, the alcohols, acetone, and glycerol. These bands are perfectly characteristic of each solvent, and their existence is regarded as strong evidence for the theory of solvation, upon which work has been in progress in this laboratory for the past 12 years.

It is difficult to see how the solvent can affect so markedly the resonance of the vibrators unless it forms some kind of a compound or system with the dissolved substance. Indeed, I am inclined to regard this evidence from the absorption spectra of solutions, for the general correctness of the solvate theory of solutions, as being so strong and unambiguous that there scarcely remains a reasonable doubt that dissolved molecules and especially ions combine with more or less of the solvent. This is especially true when we take into account the various other lines of evidence, all of which point to the same conclusion.

A large amount of work has been done on the effect of temperature on the absorption spectra of aqueous solutions, and the results are here recorded. A special form of apparatus was designed by Dr. Anderson for this work, involving the principle of total reflection from quartz prisms, which was found to work admirably. These prisms being movable in a glass trough containing the solutions, allowed different lengths of the solutions, and, consequently, very different concentrations, to be interposed into the path of the beam of light.

A piece of pressure apparatus with thick steel walls and quartz and glass ends has been devised for work with aqueous and nonaqueous solutions at high temperatures, and we are now studying the absorption spectra of such solutions at high temperatures.

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A form of apparatus has been devised which enables us to measure the intensities of the absorption bands in aqueous and nonaqueous solutions, over a range of temperature; and work is now in progress on this part of the problem.

As soon as sufficient work has been done on inorganic compounds we intend to take up organic substances and study them by the same general methods that we have used with the inorganic.

For the conductivity measurements recorded in this monograph we are indebted to Dr. A. P West and Mr. H. H. Hosford.

It gives me pleasure to express my thanks to Professor Ames for the loan of the grating used in this work, and for the ample space placed at our disposal in carrying out this investigation.

HARRY C. JONES.

CONTENTS.

CHAPTER XI. URANIUM SALTS—continued.

CHAPTER I.

INTRODUCTION.

Recent Spectroscopic Investigations.—Spectra of Gases, Spectra of Liquids and Solids, banded Spectra.—A Method of Chemical Analysis.—Atomic Structure and Spectra.—Organic Absorption Spectra, including Unit of Absorption, Theory of Chromophores, Theory of Dynamic Isomerism, and Stark's Theory.—The Complexity of Spectra.—Method of Attacking the Problem of Emission and Absorption Spectra.

The study of the various phenomena of light may be divided into three parts: The emission of light by matter, the transmission of light through space, and the absorption of light by matter. The theory of the transmission of light as an electromagnetic phenomenon was first proposed by Faraday and Maxwell. On this theory it is assumed that in all regions of space through which light passes there are electric and magnetic fields. In an electric field there exists a certain state of things that gives rise to a force acting on any electric charge that may exist there. This is the electric force and this represents the state of the region of space considered. In a similar way the magnetic field is also defined. A relation is then found between the electromagnetic quantities which is usually called Maxwell's equations, or is a modified form of these equations. Starting with these equations, Maxwell showed that the state of things represented by his fundamental equations consists of the propagation of a periodic variation of the electric and magnetic forces through space with the velocity of light. So well does the nature of these electromagnetic waves agree with the properties of light as transmitted by the ether and transparent bodies that light is at present considered to be an electromagnetic disturbance itself. The simplest case of light-waves is that of plane polarized waves traveling in the direction of the x axis. Waves of this kind are:

$$E_y = a \cos n\left(t - \frac{x}{c}\right) \qquad H_z = a \cos n\left(t - \frac{x}{c}\right)$$

E_y, the component of the electric force in the y direction, is the only component of the electric force that has a value. The magnetic force has a component only in the z direction, H_z. a is the amplitude of the disturbance, t is the time, n is the number of vibrations in a time 2π and c is the velocity of light.

RECENT SPECTROSCOPIC INVESTIGATIONS.

A light-wave in the "ether" is an electromagnetic disturbance that is propagated in free space without any distortion of form or any dissipation of energy, one of the properties of electric and magnetic fields being the power to store energy. When a light-wave strikes ordinary matter it is in general broken up into several parts. If the surface of the body is smooth, a considerable part of the energy will be taken up by a regularly reflected wave. If the surface is rough, a great number of so-called waves will be reflected. The remaining part of the disturbance will advance through the body. As no body is a perfect reflector or absolutely transparent, it follows that part of the energy of the light-wave remains with the body. This phenomenon is known as the absorption of light. We also know of many conditions of matter in which light is emitted. The object of the study of emission and absorption of light is to gain some knowledge of the mechanism of matter by which it is enabled to produce or absorb electromagnetic waves. The expression of the properties of different kinds of matter by different values of the dielectric constant (κ), the conductivity (σ) or the magnetic permeability (μ) has not been found to be satisfactory.

The electromagnetic mechanism which at present is considered as the basis of the theories of radiation and absorption is the electron. The charge which it carries has been found to be the atomic unit of electricity. Experimental results in electricity can be explained on this basis. The electron is found in the vacuum discharge-tube, in the radiations from radioactive matter, in arcs, in sparks, in secondary radiations. They are present in all bodies. By the distribution and motions of these electrons men of science to-day attempt to explain all electrical and optical phenomena. Some electrons in a conducting body are in a free state, so that they can obey an electric force. Richardson and Brown[1] have shown that ions emitted by hot platinum (and approximately so for other metals) are kinetically identical with the molecules of a gas, of equal molecular weight, at the temperature of the metal. This holds for the mode of distribution of velocity as well as its average value, and shows that the free electrons inside the metal have the same amount and mode of distribution of velocity and kinetic energy as the molecules of a gas of equal molecular weight at the temperature of the metal.

In the case of a nonconducting substance the electrons are considered as bound to certain positions of equilibrium. In a conductor in an electric field there is an excess of electrons at one end. In a dielectric, as soon as an electron is displaced from a position of equilibrium, a new (elastic) force is brought into play which pulls the electron back to its original position. The motion of electrons in nonconducting bodies, together with the change of dielectric displacement of the ether itself, makes up Maxwell's displacement-current. Under the influence of the elastic forces the electrons can vibrate about their positions of equilibrium and may thus become the centers of electromagnetic waves. In this way may be explained the emission of light and heat. Absorption results when the electrons are set into vibration by a beam of light, and part of the vibrating energy of the electron is transformed into heat energy.

As to the nature of the electron very little is known. On the other hand, the mathematical electron is much better known. As the recent experiments by Bucherer[2] on the value of e/m agree with values calculated by Lorentz, use will be made here of his conception of the electron. To each electron is ascribed certain definite dimensions. The ether is assumed

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[1] Phil. Mag., **16**, 353 and 740 (1908).

[2] Phys. Zeit., **9**, 755 (1908).

to pervade not only the space between atoms but also the space within atoms and electrons; and is also assumed to be at rest. There will be an electromagnetic field within the electron as well as without. Various distributions of charge may be assumed. Lorentz usually assumes a volume density (ρ) distribution such that ρ is a continuous function of the coördinates. The charged particle has then no sharp boundary, but is surrounded by a thin layer in which the density gradually sinks from ρ to 0. The ether is simply the space in which a certain state of the electromagnetic field exists. (Recently very interesting papers by Einstein and others on this subject have appeared.) The electron having been thus defined, equations can be formed for the electric and magnetic fields for any region in which there are electrons either at rest or in motion.

Having considered the elementary unit of the mechanism of optical phenomena, let us now turn to some of the phenomena themselves.

(*a*) SPECTRA OF GASES.

For optical purposes bodies may be divided into gases and into solids and liquids. The spectra of gases consist of an enormous number of fine lines and are usually grouped into line and band spectra. Band-spectra themselves consist of a great number of sharp lines spaced in a very regular manner, whereas line-spectra consist of lines apparently spaced more or less at random in the spectrum, although some of the lines have been found to have frequencies that are connected by certain series relations. Good examples of band-spectra are the absorption spectra of fluorine, bromine, iodine, chlorine, sulphur, or sodium vapors. These consist of thousands of very fine lines. Very interesting work has recently been done by Wood on the magnetic-rotation spectrum and the fluorescent spectrum of sodium vapor. On exciting fluorescence by monochromatic light of different wavelengths it is possible to set into vibration apparently different systems in the sodium atoms or clusters containing sodium atoms, each one of these systems of vibrators emitting a different series of bands. It is found that the presence of foreign gases has a very great effect upon the absorption spectra of sodium. The presence of hydrogen prevents fluorescence. Wood[1] found that as mercury-vapor is evolved in a vacuum the band λ 2536 broadens rapidly on the less refrangible side, attaining a width of 300 or 400 Ångström units. There is a little broadening in the other direction. If hydrogen or some other inert gas is present, the band broadens symmetrically at first. Larmor[2] has suggested that this unsymmetrical widening may be due to the formation of loose molecular aggregates, which vibrate in longer periods owing to this mutual influence. Wood and Guthrie[3] find that the cadmium absorption band λ 2288 broadens symmetrically in the case of pure cadmium but very asymmetrically when mercury is present. A very promising field for research is suggested by this work, one that will probably throw much light upon the mechanism within the atoms themselves.

Quite recently Dufour[4] has succeeded in obtaining the Zeeman phe-

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[1] Astrophys. Journ., 26, 41 (1907).

[2] *Ibid.*, 26, 120 (1907).

[3] *Ibid.*, 28, 211 (1909).

[4] Phys. Zeit., 4, 124 (1909).

nomena for many of the bands of the emission spectra of fluorides and chlorides of calcium, strontium, barium, and silicon. These give in some cases a normal and in other cases an abnormal longitudinal Zeeman (light being parallel to the magnetic field) doublet, the normal doublet usually being considered as originating from a negative charge and an abnormal doublet as due to a positive charge. The only difference in these two effects is that the light is circularly polarized in opposite directions for corresponding components of the doublet. Dufour considers that so far all spectra (emission or absorption) that show the abnormal Zeeman effect have their centers in the molecules. If one considers the explanation to be due to positive and negative electrons, then the value of e/m for these will be about the same except in the case of some of the bands of xenotine. At the University of Manchester it has been shown that the Humphrey-Mohler pressure-shift is to be observed for bands that give the Zeeman effect. With the exception of the few bands described by Dufour, the wave-length of bands is unalterable by physical and chemical changes.

The band-spectra are very complex indeed. In Watts's "Index to Spectra" the wave-lengths of over 5,000 bands are given for sulphur between λ 6400 and λ 3600, over 2,700 lines for iodine between λ 6300 and λ 5100, over 2,800 for bromine between λ 6200 and λ 5100, and over 2,600 for aluminium oxide between λ 5200 and λ 4400. Complex as these spectra are, the so-called line-spectra of the elements are even more complex. The same author gives the wave-lengths of over 2,300 lines for chromium, 3,000 for iridium, 2,300 for iron (spark), 3,000 for tungsten (spark), and 5,200 for uranium (spark). For most of these elements the greatest number of lines lie in the regions of shorter wave-lengths, and in most cases the maximum number of lines lie between λ 4000 and λ 3000. For example, Watts gives 1,100 iron lines between λ 2000 and 3000, over 1,400 lines between λ 3000 and 4000, 1,100 lines between λ 4000 and 5000, over 600 lines between λ 5000 and 6000, and only a little over 300 between λ 6000 and 6750. A similar distribution holds for vanadium, osmium, etc. The work of Schumann and Lyman shows that many more lines exist in the ultra-violet down to λ 1000, but it seems quite probable that most of the spark and arc lines lie either in the visible or in the adjacent ultra-violet regions of the spectrum.

When the source of the line-spectrum is subjected to physical changes the width and relative intensities of the bands change enormously. Rayleigh[1] and Michelson[2] have shown that the Döppler effect accounts for the width of the lines when the pressure is small. Michelson gives a formula for the breadth (b) of the spectrum lines,

$$b = \sqrt{/\theta\, m}\, \lambda(a + bd\lambda)$$

where θ is the absolute temperature, m the molecular weight, a and d constants.

At present only two physical causes are known to change the frequency of vibration of the emitters or absorbers of the line-spectrum. One of these is the Humphrey-Mohler effect—that an increase of pressure about the source

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[1] Phil. Mag., 27, 298 (1889).

[2] *Ibid.*, 34, 280 (1892).

of light causes the lines to be slightly shifted towards the red. Humphreys considers this to be due to the magnetic fields of neighboring atoms. Richardson,[1] on the other hand, considers the shift as due to electrostatic action. An increase of the partial pressure of the vapor of the emitting substance only causes the lines to widen. An increase of the total pressure of the surrounding vapor causes a shift, and this Richardson considers to be due to sympathetic vibrations set up in the surrounding atoms. If an atom is emitting light, it must be surrounded by an alternating field of force, and this will produce forced vibrations of equal period and, under certain conditions, of equal phase in the neighboring atoms. These sympathetic vibrations will then react upon the emitting atom and increase its period. After making several assumptions as to the vibrator in the emitting atom, Richardson deduces a shift which is considerably larger than that observed.

The second phenomenon of the change of frequency of line-spectra is that of the Zeeman effect. Many lines show a simple Zeeman effect such as would be produced upon a vibrating negative electron. Other lines show a very complex Zeeman effect which as yet has not been fully explained. Still other lines show no Zeeman effect at all. All line-spectra show a Zeeman effect that indicates that the vibrator carries a negative charge. Series lines usually show a similar resolution in a magnetic field as well as a similar behavior under variations of pressure, temperature, etc. Very important discussions of the Zeeman effect by Lorentz, Voigt, Ritz, etc., have recently appeared.

Some interesting work has recently been done by Lenard,[2] Stark,[3] and some others on the carriers of matter that are emitting light. In vacuum-tubes, in arcs, in flames, and in the radiations from radioactive bodies we have electrons, atoms, molecules, charged atoms or molecules, or aggregations of these that are moving in some cases with very great velocities. The free electron, as we shall see, radiates a continuous spectrum, but the bound electron, being disturbed comparatively infrequently by collisions of the atom in which it is bound, will emit more or less monochromatic radiations. Now, in the case of flames, arcs, etc., it is possible to separate the positively and negatively charged ions by means of an electric field.

Lenard's work indicated that the radiators of line-spectra were either neutral atoms of positive ions, the principal series being due to neutral atoms, and the subordinate series to positively charged atoms. If an ion has a swarm of molecules about it, it is unable to radiate or absorb. Stark studied the Döppler effect of canal-rays in vacuum-tubes. He found that in the case of a beam of light coming from the canal-rays in the same direction in which they are moving, many spectrum lines showed a "rest" line and a displaced line due to the Döppler effect. He found that some series lines consisting of doublets originate from univalent positive ions and the mercury triplets start from divalent positive ions. Some lines show no Döppler effect and these originate from a negative electron joining a positive ion. The displaced line is separated from the normal line by a dark space

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[1] Phil. Mag., **14**, 557 (1907).

[2] Ann. Phys., 9, 642 (1902); **11**, 649 (1903); **12**, 475, 737 (1903).

[3] *Ibid.*, **14**, 506 (1904).

which is found to be wider the smaller the wave-length of the line. Assuming that there are particles of varying velocities in the canal-rays, Stark concludes that a certain velocity is necessary before a particle begins to radiate light appreciably. Stark thus considers velocity of translation as one cause of radiation. The other cause of continuous radiation of energy by an atom is frequent collision with electrons or other charged atoms.

So far no satisfactory model has been devised that will act as a source of spectrum lines. No system that includes electrical charges in orbital motion is permanent on account of their radiation of energy. The favorite and best model consists of systems of coaxial circular rings of equidistant electrons, but even in this case Schott [1] has shown that such a model (in particular that of Nagaoka), although giving a large number of spectrum lines, is too unstable to produce wave-trains of sufficient length.

Stark has recently suggested the possibility of explaining a positive charge as due to negative electrons revolving in circular orbits, the centers of these circular orbits being themselves on a circle. By means of such a device a positive charge can easily be explained. He thinks that line-spectra originate from a system of this kind. The general trend [2] of opinion seems to favor the view that spectrum lines are due to some special mechanisms in the atom which are set in operation during ionization and operate for only a short time. At any one time the atom may be radiating light of but one frequency.

(*b*) SPECTRA OF LIQUIDS AND SOLIDS.

The optical phenomena of gases are so much better understood on account of our more perfect knowledge of gases that considerable space has been given to their discussion. On the other hand, the conditions in liquids and solids are so exceedingly complex that at present our theories are in the main very crude. Considerable advances in our experimental knowledge of these phenomena have recently been made and a short summary of these will be given.

The spectra of liquids and solids can be roughly divided into the continuous spectra emitted by very hot liquids or solids, secondary X-ray radiations, phosphorescent or fluorescent spectra, and the absorption or emission of a banded spectra.

According to the present theory, X-rays, and possibly γ-rays, and the continuous spectra from hot liquids and solids are due to a rapid and irregular succession of sharp electromagnetic pulses, each of which is due to the change of velocity of electrons. Recent work on X- and γ-rays indicates that in most bodies a certain homogeneous secondary radiation is excited when the body is exposed to the X- and γ-rays. This secondary radiation seems very similar to the phosphorescent bands of the compounds investigated by Lenard and Klatt [3] and others. Lenard and Klatt [3] consider that electrons can exist in three different states—in a "free" state, as in the metals

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[1] Phil. Mag., **15**, 438 (1908).

[2] J. J. Thomson: "The Corpuscular Theory of Matter" (1907). Ladenburg and Loria: Nature, 79, 7 (1908). Eagle: *Ibid.*, 79, 68 (1908).

[3] Ann. Phys., **15**, 451 (1904).

where they take part in conduction; a "liquid" state where there is a state of motion sensitive to light vibrations; and a "solid" state where the electrons take part in neither conduction nor the absorption of light. They consider that in the states of aggregation which cause phosphorescent bands there are certain places in the atoms, dynamids, where electrons can be stored at low temperatures. To each phosphorescent band there correspond then these phases: (1) an upper momentary or heat phase; (2) a permanent phase; and (3) a lower momentary phase. For a great many bands they succeed in obtaining these three phases when they change the temperature sufficiently. The temperature of solid hydrogen is sufficiently low to bring most of the phosphorescent bands into the lower momentary phase. In this phase the electrons ejected from the metallic atom by photoelectric influence of illumination are fixed and stored in the neighborhood, only a few returning immediately, and these produce the "momentary light" observed during illumination. In the permanent phase the electrons are stored for a certain time in the dynamids and eventually return to the metallic atom.

Various theories have been proposed to explain the more or less general absorption throughout large regions of the spectrum. Drude[1] considers that in general ultra-violet bands are due to the absorption of electrons, and infra-red bands to the absorption of ions. Houstoun,[2] Pfund,[3] and others support this view.

(*c*) BANDED SPECTRA.

By banded spectra we shall in general designate bands which at low temperatures become quite fine, such as the uranyl, neodymium, or erbium bands. As the present paper deals with only a small range of temperature and concentration and but one solvent, a full review of previous work will not yet be given. Rudorf and Washburn have given a very good review of this subject from the hydrate point of view.

Brewster observed, in 1831, that the transparency and color of many solids change when they are heated. Schönbein, in 1852, states that many bodies become more highly colored at higher temperatures while at low temperatures they lose their color. He found that sulphur is colorless at −50° C. and bromine at −70° C. Moissan and Dewar, in 1903, found that fluorine becomes colorless at −253°, so that at low temperatures chlorine, bromine, iodine, and fluorine are colorless.

Conroy (1891) found that the bands of cobalt glass are displaced towards the red with rise in temperature. Rizzo (1891) found similar results with glasses containing cobalt, didymium, and manganese. Königsberger (1901) found the curve of absorption to be displaced towards the red with rise in temperature, but concluded that the maximum of absorption was not changed. This applied to the wider bands. The fine bands showed no displacement between 10° and 500° C. Hartley investigated the absorption spectra of a large number of solutions between 0° and 100°. He inter-

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[1] Ann. Phys., **14**, 677–725, 936–961 (1904).
[2] Proc. Roy. Soc., 606 (1909).
[3] Astrophys. Journ., **24**, 19 (1906).

preted his results from the point of view of hydration. Houstoun investigated the bands of glasses containing uranium and neodymium but found no shifts of the bands.

Very important papers on this subject have been published by Becquerel, Ritz, Retschinsky, Stark, Bois and Elias, Königsberger and Kilchling, Page, Laub, Voigt, and others.

A METHOD OF CHEMICAL ANALYSIS.

The stimulus to research along many lines in science is often very much augmented by the requirements of technology. This is especially true in connection with many branches of organic chemistry. A good example is the case of the pure food laws. In regulating the use of various coloring and preserving matters added to foods, it is necessary that the examiners shall be able to recognize various compounds easily and quickly. Many organic compounds possess very characteristic colors, and it has often been asked whether the absorption spectra of these compounds would aid in their detection. Our present knowledge of absorption spectra is limited chiefly to the visible region of the spectrum. Before this method of analysis can be satisfactorily used by chemists it will be necessary to measure the absorption throughout the region of the infra-red. At present a few potassium salts have been studied in the regions of wave-lengths as long as 0.1 mm. (The shortest electromagnetic waves that are produced by mechanical apparatus are about 6 mm. in length.)

The analysis of inorganic compounds by means of their spectra is probably less hopeful, although the absorption or reflection spectra would often be very useful. A great many of the inorganic cations show characteristic absorption in the visible portion of the spectrum, and practically all have bands in the infra-red. J. Formanek[1] has suggested that the absorption spectra of metallic compounds of alkannin would serve to indicate the presence of the metals.

The following measurements of the absorption bands of different compounds of alkannin show the effect of the metal upon the position of the bands.

	λ	λ		λ	λ
Uranium	6870	6315	Lithium	6210	5745 5340
Iron	6545	6030	Nickel	6192	5725 5320
Potassium	6387	5910	Calcium	6147	5682 5276
Cobalt	6370	5845 5405	Copper	5953	5515 5128
Sodium	6337	5857	Aluminium	5857	5425 5048
Barium	6281	5805 5395			

The use of absorption and emission spectra has been most successful in separating the rare earths. The method has been used by Crookes, Becquerel, Exner, Demarçay, and many others. A very good account of this work has been given by Böhm.[2] Recently Urbain[3] has used the phosphorescent spectra to purify compounds of europium, gadolinium, terbium, dysprosium, neoytterbium, and lutecium.

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[1] Die Qualitative Spectralanalyse anorganischer Körper.

[2] Die Darstellung der seltenen Erden, Leipzig (1905).

[3] Le Radium, June (1909).

ATOMIC STRUCTURE AND SPECTRA.

The greatest interest, however, lies in the relation between chemical constitution and absorption or emission spectra. The relation between the flame, spark, or arc spectra and the chemistry of the emitters is not known. The source of spectra, like that from the blue cone of a Bunsen burner, the Swan spectra, is at present unknown. It is very probable, however, that chemical reactions play an important rôle in the emission or absorption of light and especially of band-spectra. We usually think of most spectra like the sodium *D* lines as coming from the metallic atoms of sodium. Fredenhagen[1] points out that under most conditions oxygen is present. In chlorine, hydrogen, or fluorine flames, calcium, strontium, thallium, sodium, barium, and copper give spectra that are very different from those obtained when oxygen is present. Thallium under these conditions does not show the characteristic green line, and the *D* sodium lines are completely absent. Work upon the absorption of sodium, mercury, potassium, and various other vapors shows that the presence of foreign gases modifies the character of the absorption very much. Many believe that certain series or groups of lines are due to chemical reactions of various kinds.

Chemical reactions and processes of ionization and recombination are believed to place the atom or molecule in a *peculiar condition* by means of which it can emit energy to the ether or absorb energy from it. Under ordinary conditions the atom does not seem capable of doing this. In sodium-vapor, for instance, theory indicates that only one in several thousand of the sodium atoms are taking part in the absorption of the *D* lines at any particular instant. The problem as to how energy is transferred to and from matter is then one of the fundamental problems of science.

Our present theory of the mechanism of absorption and emission of radiations is very simple. Light and heat are electromagnetic radiations, and hence the emitter or absorber must be either an electric charge or a magnetic pole. As free magnetic poles are not known to us and free electric charges are, theory makes the electric charge the origin of all electromagnetic phenomena. At present no positive electrical charge is known to be associated with portions of matter smaller than the hydrogen atom, whereas negative charges or electrons are known to be associated with charges of about one seventeen-hundredth that of the hydrogen atom. As far as experiment shows, these electrons always have the same properties and the same charge, no matter from what element they may come. It is for these reasons that the electron is made the basis of all electromagnetic theory, and at present there are but few phenomena that can not be explained, if explained at all, by this theory.

Radiations, and especially light-radiations, have, then, their origin in electric charges. Continuous spectra like those of the metals are due to free electrons in the metals and have little connection with chemical constitution. Fine line- and band-spectra apparently are due to different systems of electrons within the atom, and are greatly affected in intensity

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[1] Phys. Zeit., 8, 404, 729 (1907).

by the presence of neighboring atoms. The electrons of this type vibrate in definite frequencies that can be changed by only infinitesimal amounts.

ORGANIC ABSORPTION SPECTRA.—THE UNIT OF THIS ABSORPTION.

In discussions concerning the color of organic compounds it is customary to speak of the selective absorption as being due to certain ions or molecules. This is probably true in the infra-red; the electric charges absorbing these long wave-length radiations being probably associated with masses of molecular size. But in the visible and ultra-violet portions of the spectrum the absorber invariably has a value of e/m (e the charge, and m the mass) of the same magnitude as that of the electron. Drude[1] has investigated a large number of organic compounds and shows that the absorber of all the shorter waves of the spectrum is the negative electron. Houstoun[2] has calculated the value of $e/m = 1.297\ \gamma\ \kappa \frac{\lambda_1 - \lambda_0}{\lambda_0^3}$ for the absorption bands of several organic compounds and also shows that the absorber is the electron. (γ is the refractive index, κ the maximum value of the coefficient of extinction; λ_0 is the wave-length of maximum absorption, and λ_1 is the wave-length for which the coefficient of extinction has a value equal to half its maximum.) The formula used is based on the present laws of dispersion.

The following table is taken from Houstoun's paper.

Compound.	λ_0	e/m
Fuchsin in alcohol	5500	$1.8\ (10)^7$
Phloxin in water	5150	$1.4\ (10)^7$
Crystal violet in alcohol	5750	$4.9\ (10)^7$
Corallin in alcohol	4650	$1.6\ (10)^6$
Methylene blue in water	6650	$5.4\ (10)^6$
Water blue in water	5750	$8\ 1\ (10)^6$
Eosin blue in water	5150	$6.9\ (10)^6$
Cyanine in alcohol	5870	$5.8\ (10)^6$

Throughout this monograph, then, it will be considered that the absorbers are negative electrons. These electrons have certain free periods corresponding to bands of selective absorption. These free periods are greatly modified by the presence of certain chemical radicles, and seem to be electrons that are situated either in the outer parts of the atom or between two or more atoms. Stark and others call these the valency electrons and consider that chemical valency is due to them. Chemical bonds and these electrons will therefore be closely related. As an aid to our imagination we will consider the atoms or ions as large spherical regions throughout which a positive charge is uniformly distributed. These regions are somewhat similar to the "spheres of influence." Two atoms collide when their spheres of influence touch one another. Groups of atoms comprising ions, radicles, or molecules will also have spheres of influence. No ion can pene-

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[1] Ann. Phys., 14, 677, 726, 936, 961 (1904).

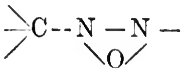
[2] Nature, **80**, 338 (1909); Proc. Roy. Soc., A, **82**, 606, Sept. 18 (1909).

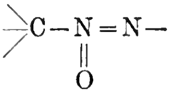
trate the sphere of influence of another atom or molecule. On the other hand the electrons are very small and compare in relative size to the atom much as the sun compares in size to the solar system. Electrons can, therefore, move through ions and atoms or can move in the interatomic spaces with considerable ease. In the metals a large number of electrons are free. In organic compounds that are transparent to certain wave-lengths the electrons, in general, will be held within certain regions by forces that are elastic in their nature; that is, the force increases in proportion to the amount the electron is moved from its position of equilibrium.

THE THEORY OF CHROMOPHORES.

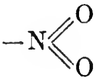
In considering absorption spectra it is often quite sufficient to speak qualitatively of the color of different compounds. The introduction of certain groups into colorless compounds often results in a colored compound. Any such group is a chromophore. Sometimes the chromophore may be weak and it may require the addition of several chromophores to produce a colored compound. Ultimately the color is due of course to absorbers existing within the chromophore. Among the better known chromophores are the groups:

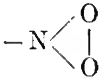
$>C=C<$ $=CO$ $>C=NH$ $-CH=N-$ $-N=N-$





$-N=O$





$=N=O$ $=C=S$ $-C-S_2-C-$

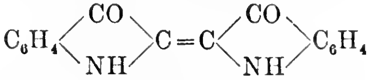
The structure of compounds is very intimately connected with their color, and by means of color differences it is often possible to differentiate isomers. An example of the latter case is the following:

$C_6H_5 \cdot N=N \cdot SO_3K$	$C_6H_5 \cdot N=N \cdot SO_3K$
Syn-benzene-diazo-sulfonate, orange.	Anti-benzene-diazo-sulfonate, yellow.

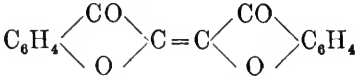
The following are typical examples of the effect of chromophores:

Colored.		*Colorless.*	
$C_6H_5-N=N-C_6H_5$	Azobenzene.	$C_6H_5NH-NHC_6H_5$	Hydrazobenzene.
$C_6H_5-N=O$	Nitrosobenzene.	$C_6H_5-N \cdot H \cdot OH$	Phenylhydroxylamine.
$O=C_6H_4=O$	Quinone.	$HO \cdot C_6H_4 \cdot OH$	Hydroquinone.
$C_6H_5 \cdot CO \cdot CO \cdot CO \cdot C_6H_5$	Diphenyltriketone.	$C_6H_5 \cdot CO \cdot CH_2 \cdot CO \cdot C_6H_5$	Dibenzoylmethane.

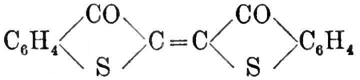
The introduction of a radical into an organic compound usually either weakens the color or increases it. An interesting question comes up as to whether color-changes are in any way related to energy changes in these chemical reactions. A bathochrome causes the absorption bands to be wider, while an auxochrome causes the intensity of the absorption to be greater. A hypsochrome causes the absorption bands to narrow, a diminochrome causes the coefficient of absorption within the band to be smaller. A good example of an auxochrome is that of the group $-CO-C=C-CO-$ in indigo:



A similar rôle is played by the same auxochrome in the deeply colored compounds similar to the indigos:



and



Alkyl, aryl, and the halogens act as bathochromes; while the acylenes CH_3CO and C_6H_5CO act as hypsochromes. Krüss has shown that CH_3, OCH_3, C_2H_5 and Br shift the absorption bands to the red, NO_2 and NH_2 towards the violet.

In general, the color, the position of the absorption bands and the extinction coefficients vary for different solvents. In many cases a very plausible explanation is to assume the formation of chemical compounds between the dissolved salt and the solvent.

Benzene and its derivatives show selective absorption in the ultra-violet. In alcohol the benzene absorption consists of seven bands between λ 2330 and λ 2710. The absorption and fluorescent spectra of a large number of compounds containing the benzene ring have been investigated. A good example is that of anthracene. This shows the following fluorescent bands.

Solid........	λ 4250	λ 4495	λ 4745	λ 4980	λ 5300
Solution.....	λ 4050	λ 4275	λ 4540	λ 4820	....
Vapor.......	λ 3900	λ 4150	λ 4320	....	....

Benzene gas has some 30 bands. In solution the bands are broad.

The bands of both the vapor and solution are, in general, shifted to the red when chlorine, bromine, the methyl group, etc., replace the hydrogen. The shift is greater the greater the molecular weight of the entering atom or group. The bands of benzene that are shifted are those that are common to benzene, toluene, ethylbenzene, and oxyxylene, and are unaffected by temperature and pressure.

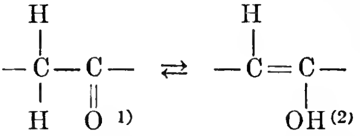
Hartley gives the following wave-lengths for these bands:

In solution..	λ 2682	λ 2657–2642	λ 2614–2600	λ 2539	λ 2480	λ 2426.5	λ 2376
In vapor....	λ 2670	λ 2630	λ 2590	λ 2523	λ 2466	λ 2411	λ 2360

The substitution products of benzene have much less characteristic spectra than benzene itself.

THEORY OF DYNAMIC ISOMERISM.

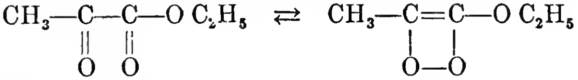
Baly and others have recently supported the view that the absorption of light by organic compounds does not take place under ordinary conditions, but that absorption takes place when there is a change in the way in which the atoms are united, as when a chemical compound is transformed into an isomeric form. This dynamic isomerism is known to take place in many chemical compounds in the presence of a catalytic agent or at high temperatures. The case of acetylacetone and ethyl acetoacetate is cited as an example. The absorption in this case is considered as being due to the reaction changing the ketonic (1) to the enolic (2) form.



$$-\underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}-\underset{\displaystyle O}{\underset{\|}{C}}-\ {}^{1)} \rightleftarrows -\overset{\displaystyle H}{\overset{|}{C}}=\underset{\displaystyle OH}{\underset{|}{C}}-\ {}^{(2)}$$

It has been found that anything that changes the velocity of the above reaction also changes the persistence of the absorption bands.

The case of pyruvic ester is also given as a typical example of this kind of a reaction which results in the absorption of light.



$$CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}-O\,C_2H_5 \rightleftarrows CH_3-\underset{\displaystyle O}{\underset{|}{C}}=\underset{\displaystyle -O}{\underset{|}{C}}-O\,C_2H_5$$

This oscillation of the carbonyl grouping Stewart and Baly call isorropesis.

On account of the large number of isomeric compounds that may exist among the hydrocarbons, it is easily seen that a theory of this kind may have very wide applicability.

THEORY OF STARK.

Stark considers that chemical valency can be explained as due to the presence of negative electrons between the atoms, or rather the positively charged ions that constitute atoms when they are combined with one or more electrons. These valency electrons are considered as being "locked" to the atoms in different degrees. Whenever a double chemical bond exists in a compound it is considered that one or more of the valency electrons is very loosely united with the atom. Under certain conditions, as, for example, when ultra-violet light falls on a compound, some of the electrons may absorb sufficient energy to be shot off from the molecule. In this way the photoelectric is explained. When an electron is attracted back to a molecule which has lost one, Stark supposes that light will be emitted, and in this way fluorescence can be explained. The fluorescence of a large number of organic compounds has been investigated by Stark and Steubing.[1]

COMPLEXITY OF THE PROBLEM OF THE SPECTRA OF COMPOUNDS.

It is a fact that investigations on the spectral emission and absorption of bodies have been far less fruitful in extending our knowledge of the structure of the atom than had been expected. This is largely owing to the almost infinite complexity of the structure of the atom and our general ignorance of the forces that exist there. Probably the best known example is that of the uranyl group which we shall describe. Let us consider the spec-

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[1] Phys. Zeit., 9, 661 (1908); 9, 481 (1908).

tral vibrations that can be produced by components that exist or may be produced from the apparently simple UO_2 group:

(1) We have the absorption spectrum described above. At low temperatures most of these bands break up into much finer bands.

(2) The uranyl salts under various methods of excitation emit a phosphorescent spectrum of a large number of rather fine bands throughout the visible region of the spectrum. It is quite possible that this spectrum is intimately connected with that of the absorption spectrum.

(3) We have the absorption spectrum of the uranous salts which has been described above. This spectrum has been probably caused by the change of valency of the uranium atom. Uranium is known to form quite a large number of oxides, and it is quite possible that for each valency of the uranium we have a characteristic spectrum. (This also is being investigated.) It is also quite probable that at lower temperatures those spectra would consist of quite fine bands.

(4) We have the spark spectrum and the absorption spectrum of oxygen, and

(5) that of ozone, which bears no relation to that of oxygen.

(6) There is the exceedingly complex spark spectrum of uranium, consisting of thousands of fine lines, and also

(7) the complex arc spectra. From radioactive experiments it is known that uranium is continually breaking down into ionium.

(8) Ionium possesses the properties of a chemical element and most likely has a spectrum of its own. This would make eight spectra.

(9) Ionium breaks down into radium and radium has a very characteristic spark spectrum, as does also

(10) the radium emanation. During the various radioactive transformations several a-particles are emitted with a velocity almost as great as that of light. It is probable that these particles are moving with very great velocities in the uranium atom under ordinary conditions.

(11) The a-particles are known to be charged helium atoms and therefore under proper excitation would give the helium spectrum. The radium emanation breaks down into radium A, B, C, D, E, and F. These products behave like chemical elements and probably have characteristic spectra.

(12) The final product is lead, which has very complex spark and arc spectra. During these transformations several electrons have been thrown off from the various products with enormous velocities. In a very large number of the above spectrum lines the Zeeman effect indicates the presence of negative electrons and charged doublets.

We thus see what an extremely complex system the group UO_2 must be, and it might seem almost hopeless to disentangle the mystery of its various spectra. At present we know that the arc- and spark-spectra problem is very complex and that we have very few methods of producing any changes in them. Practically the only method of changing the frequency of these vibrations is by applying a very powerful magnetic field or great pressure and these changes in the frequency are very small. One very important result, however, has been obtained by Kayser, Runge, Wood, and others. This work consists in separating spectrum lines into various series. A series of lines comprises those whose intensity and Zeeman effect vary in the same way when the conditions outside the atom are changed. The work of Wood is important as showing that spectrum lines are due to different systems of vibrators inside the atom. By using monochromatic light of different wave-lengths he has been able to excite different series of lines which constitute altogether the fluorescent spectrum of the element.

Present theories of the atom usually regard the electrons and other vibrators that are the sources of arc and spark lines as being well within the atom, and as affected by external physical conditions only under very special circumstances. Stark believes that these electrons may rotate in circular orbits, the locus of the centers of these orbits being a closed curve, say a circle. This system will be equivalent to a positive or negative charge according to the sense of rotation of these electrons. These electrons we will call ring electrons. Supposing these systems to be positive charges, it will require electrons to neutralize these charges. Several of these neutralizing electrons may be in the outer parts of the atom and under certain conditions might be knocked off from the atom. These easily removable electrons will be called "valency" electrons, and can exist under different conditions of "looseness" of connection with the atom. Most of the neutralizing electrons will probably lie far within the atom. For instance, we would expect that in the uranium atom the charged helium atoms are neutralized by negative electrons.

Our theory is that the finer absorption bands of such salts as neodymium, erbium, and uranium are due to vibrations of these neutralizing electrons, and that the forces acting upon these are considerably different from those acting on the ring electrons, which, in many cases, give a normal Zeeman effect. It is probable that these neutralizing electrons play the greatest rôle in the optical properties of bodies, such as the properties determining the index of refraction, the extinction coefficient, etc.

Usually the equation of motion of such an electron is given by an equation like the following when a light-wave of an electric field E cos pt is passing by it:

$$m\frac{d^2x}{dt^2}+k\frac{dx}{dt}+n^2x=E\cos pt$$

where m is the total mass (electromagnetic and material) of the electron, $k\,dx/dt$ is the damping or frictional term, and n^2x is the quasi-elastic force. It is an experimental fact, as shown by the above work and the work of other investigators, that k and n^2 are not only functions of the electron and the atom, but that they are also functions of the physical and chemical conditions existing in the neighborhood of the atom.

On the other hand, the effect on k and n^2 for a ring electron, when external physical and chemical conditions are changed, is very small. It is for this reason, and the probable fact that there are relatively few neutralizing electrons, that we believe that much greater progress can be made in determining some of the properties and constitution of various interatomic systems of atoms and molecules by the study of the absorption spectra of uranium and neodymium than by a study of the arc- or spark-spectra of the same.

METHOD OF ATTACKING THE PROBLEM OF EMISSION AND ABSORPTION SPECTRA.

The method of attacking the above problem will be to study the effect on the spectra of a body produced by changing the physical and chemical conditions about the light absorbers or emitters within as wide ranges as possible. Some of the possible changes that can be made are as follows: Take, for instance, the uranyl group UO_2. We can find the effect upon the absorption bands produced (1) by diluting the solution, (2) by changing the acid radical to which the uranyl group is united, (3) by changing the solvent and using mixtures of solvents, (4) by adding other salts (like aluminium chloride), or (5) by adding acids of the same kind as that of the salt of the uranyl group. The effect (6) of adding foreign salts and acids at the same time and then varying the solvent, or the temperature, can also be tried. In this way a very large number of very interesting things can be tested. In most of these changes *lc* will be kept constant.

In the above example the temperature (7), the external pressure (8), the electric field (9), and the magnetic field (10) can be changed between wide limits. The latter effect is a very important one. For example, in aqueous solution neodymium salts give a large number of fine bands, in glycerol there are quite a number of new bands replacing the "water" bands, and in the alcohols there are various "alcohol" bands. At low temperatures these bands become very fine and it is quite possible to detect the Zeeman effect. Now it seems quite probable that a "glycerol" band and an "alcohol" band that seem to replace each other as the solvent is changed are both due to the same vibrator. If the Zeeman effect is the same in both cases it would be a strong argument in favor of the above theory. A case that will soon be described is very important. It was found that the wave-lengths of certain neodymium lines in a pure aqueous solution did not change when the temperature was raised from 0° to 90°. If, however, calcium chloride was added, then on raising the temperature the above bands were shifted to the red. A very interesting and important investigation is whether the Zeeman effect on the band would be affected by the presence of substances like calcium chloride.

To be compared with the above changes are changes in the absorption spectra of the crystals of the salt (11) as affected by water of crystallization, or by the presence of foreign substances, or as affected by the polarization (12) or direction of passage of light through the crystal. The absorption spectra (13) of the anhydrous powder at different temperatures, etc., should be found. The phosphorescent spectrum (14) should be studied in this connection, especially as affected by the mode of stimulation (X-rays, cathode rays, heating, or monochromatic light of different wave-lengths). The temperature, electric or magnetic field could be changed about the phosphorescing body. The effect of change of state (15) should be tried if this is possible, also any possible changes of valency of the atoms (16) composing the body investigated. It is very important that these suggested modes of attack should be extended throughout the whole range of wave-lengths.

After correlating the data obtained by the above-named investigations it is pretty certain that it will be possible to take each vibrator and trace the effects produced upon it by the above changes. It is highly probable that we shall also know something of the nature of the vibrating system and the part that it plays in that complex body we call the atom.

For instance, let us take the bands of uranyl nitrate. It was found that the uranyl bands of an aqueous solution of the nitrate had shorter wave-lengths than that of any other uranyl salt in water. The uranyl bands of the nitrate in other solvents were farther towards the red than the bands of an aqueous solution. Now, although the solvent has a great effect upon the bands, nevertheless it seems quite certain that the NO_3 group has a very considerable effect upon the vibrations of the uranyl group. If it were possible to find the ratio e/m for the vibrators in this case by the Zeeman effect, it might be possible to find an approximate value for the force exerted by the NO_3 group upon the vibrator. It seems quite certain that this force differs for the vibrators producing different bands. The measurements of the wave-lengths of the uranous bands are as yet very few, yet they seem to indicate that for aqueous solutions of the uranous salts the bands of the nitrate are farther towards the violet than the bands of the other uranous salts. The values given for the phosphorescent bands by E. Becquerel and by J. Becquerel indicate that the bands of the nitrate are further towards the violet than those of the other uranyl salts. We thus see that throughout these three spectra the NO_3 group exerts a similar force upon the vibrators that are the cause of the bands.

CHAPTER II.

EXPERIMENTAL METHODS.

In this work the methods used by Jones and Uhler[1] and Jones and Anderson[2] have in the main been employed.

The investigations of the effect of changes in temperature on the absorption spectra of solutions have been confined to different concentrations of aqueous solutions of the chloride, nitrate, acetate, sulphate, and sulphocyanate of cobalt, the chloride, acetate, and sulphate of nickel, the chloride, sulphate, and acetate of chromium, chrome alum, the nitrate and bromide of copper, uranous chloride, erbium chloride, the chloride and nitrate of praseodymium, the sulphate, acetate, chloride, and nitrate of uranyl, and the chloride, bromide, and nitrate of neodymium. Spectrograms of the absorption spectra for a given concentration of a salt, with a constant thickness of layer, have been made for every 15° between 0° and 90° C.

To make a spectrogram, light from a Nernst glower and from a spark is allowed to pass through the solution that is being investigated. It is then focused upon the slit of a spectroscope, and, falling on a concave grating, is spread out into a spectrum on the film upon which it is photographed. The films used were made by Wratten and Wainwright, of Croyden, England, and were very uniformly sensitive to light from λ 2100 to λ 7200.

The sectional diagram (fig. 1) will make the experimental arrangement of the apparatus clearer. N is a Nernst glower which is arranged to slide along the rod AB. P and P' are quartz prisms which are held by a lid L. The prism P is stationary, whereas the prism P' can be moved by the traveling carriage E back and forth through the trough T, which contains the solution whose absorption spectrum is being investigated. AB is so inclined that the optical length of the light-beam from N to P', P and the concave mirror M shall be constant, whatever the length of the solution between P and P' may be. The greatest length of path PP' used was 200 mm. The hypothenuse faces of P and P' are backed by air films which are inclosed by glass plates cemented to the quartz prisms.

Considerable difficulty was experienced in finding a cement that would adhere to the polished quartz prisms at the higher temperatures. For aqueous solutions baked caoutchouc was found to work fairly well. Among the various cements that may prove successful is bakelite.[3] This is briefly described as being made of equal amounts of phenol and formaldehyde to which a small amount of an alkaline condensing agent is added. This latter is a compound made of ammonium carbonate, soap, sodium carbonate,

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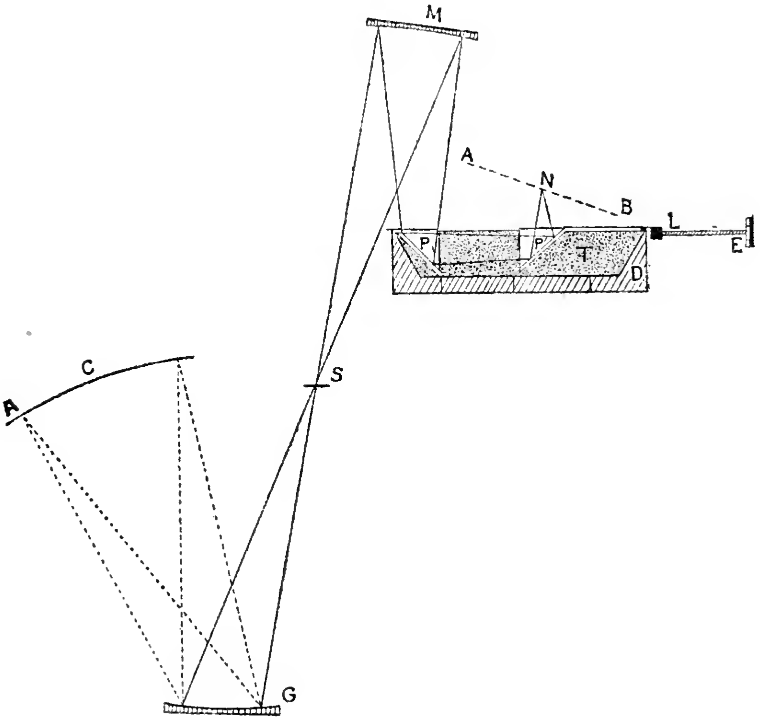
[1] Carnegie Institution of Washington Publication No. 60.

[2] *Ibid.*, No. 110.

[3] Journ. Ind. and Eng. Chem. (March), p. 156 (1909).

and potassium cyanide. The solution should be gently heated. The lower layer of liquid is used for the cement and is heated for several hours at a temperature of 160° under the pressure of 100 pounds per square inch.

D is a brass box holding the trough *T*. *D* is filled with oil and is placed in a water-bath whose temperature can be varied between 0° and 90° C. The path of the beam of light is then from the Nernst glower *N* or spark to the quartz prism *P′*. The light is totally reflected from the hypothenuse face of this prism through the solution to *P*. This prism also has its hypothenuse face backed by an air-film, so that the light is totally reflected upwards to the concave speculum mirror at *M*. *M* focuses the light on the slit of the Rowland concave grating spectroscope, *G* being the grating and *C* the focal curve of the spectrum. The prism arrangement was designed by Dr. John A. Anderson.



When the quartz prisms were being set up for temperature work a very peculiar set of images were obtained that the writers have not yet fully understood, although the optics is probably quite simple. When a Nernst filament is observed through one of the prisms so that the incident beam of light is symmetrical to the prism, there is but one image of the filament to be seen. If now the prism is rotated in general three images will be seen. For a certain position of the prism the three images are of practically the same intensity.

This apparatus was found to work very well for aqueous solutions. Some evaporation took place at the higher temperatures, but distilled water was added in proper quantity and mixed with the solution so as to keep the concentration constant. By using troughs of different lengths it was possible to vary the length of salt solution through which the light beam passed from 1 to 200 mm. One inconvenience was experienced at low temperatures; moisture would sometimes condense upon the exposed prism-faces. To overcome this an air-blast was directed upon these faces, and this helped very materially to prevent the condensation of moisture.

For the investigation of glycerol and other solutions a cell made of fused silica was used. The cell, as received from the Silica Syndicate Company, did not have plane parallel ends. At the suggestion of Dr. Pfund these were ground down with finely powdered emery and rouge. In this way a very serviceable cell was obtained. The depth of liquid in the cell was 104 mm.

For work on the effect of high temperatures on absorption spectra, a closed steel cell is being made. This is intended to stand the pressures exerted by the alcohols, acetone, ether, water, etc., at their critical temperatures. The ends contain quartz windows and the whole interior of the cell will be lined with gold. At the same time a radiomicrometer is being made and an apparatus is being devised by means of which quantitative measurements of the energy absorption for all parts of the spectrum can be obtained.

In the case of solids, the time of exposure is necessarily long, usually occupying several hours. It is very necessary in this case to screen off stray light. The method is very simple, consisting in focusing by means of mirrors or lenses the light from a Nernst glower or an arc upon the salt. The salt is placed a short distance from the slit of the spectroscope, so that the directly reflected light does not enter the slit. By this means only the diffusely reflected light enters the slit, and in general this light has penetrated somewhat into the salt and, accordingly, some wave-lengths are partly or wholly absorbed. The salt is placed at such a distance that the grating is completely filled with the beam of diffusely reflected light entering the slit. This method has been used by several investigators, notably by Anderson[1] and Schultz.[2]

The observations on the phosphorescence of uranium compounds were made with the Hilger spectroscope, from which wave-lengths can be read directly. Either sunlight or the light from a spark was used as the source of light by means of which the phosphorescence could be excited. Screens of variously colored glasses were used in order to find whether the wave-length of the exciting light had any effect upon the phosphorescent spectrum. Especially valuable was a glass screen[3] that absorbed all wave-

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[1] Astrophys. Journ., **26**, 73 (1907).

[2] Diss., Johns Hopkins University, June (1908).

[3] This glass screen is very useful for observing Haidinger's brushes. These brushes as seen by the naked eye are yellow and purple. Using a blue-glass screen the yellow fringes become dark and show no color. With the above-mentioned screen the brushes are red. These facts corroborate the theory given by G. G. Stokes: Collected Papers, **2**, p. 362.

lengths except the red, blue, and violet. When this was used no yellow or green light fell upon the phosphorescing uranium salt, so that any light in the yellow and green was necessarily due to phosphorescence and not to reflection. A Fuess monochromatic illuminator was also used, sunlight or arc-light being focused upon the slit of the illuminator. The salt was placed in the beam of transmitted light. Usually the region of spectrum used was 50 or 100 Ångström units wide. The phosphorescent light was viewed with the Hilger spectroscope.

In the work on the Zeeman effect, the large electromagnet described by Reese was used. This electromagnet has very large pole-pieces. A cell to hold the solution was made of thin cover-glass plates about 1.2 by 1.2 by 0.3 cm. in size. The light from an arc or a Nernst glower was focused upon the solution by means of lenses, and the emergent beam of light focused upon the slit of the spectroscope.

The concave grating described above was used for mapping the absorption spectra of solutions. A plane Rowland grating was also employed for visual work in the second and third orders of the spectrum. For polarizing the incident light Nicol prisms were used.

When anhydrous salts were employed they were dried in every case by the best methods available. Thus, chlorides were dried in a current of hydrochloric acid, bromides in a current of hydrobromic acid gas, and so on.

The usual precautions were taken in working with nonaqueous solvents to keep out all traces of moisture. Dehydrated salts were, of course, protected from contact with the air.

An attempt was made to obtain the electrostatic Zeeman effect. For solutions condensers made of ordinary cover-glass slides (used in mounting sections for microscopic examination) were used. Aluminium foil was placed between the glass slides in alternate layers. The solution (for instance, neodymium chloride in glycerol) to be investigated was placed between the slides between which there was no foil. For the production of an electric field a Holtz machine was employed. This experiment was tried for several solutions and for one gas, nitric oxide. In no case could any difference be observed when the electric field was on and when it was off. Further work is being done in this direction, especially on gases such as iodine, bromine, nitric oxide, etc. In this way enormous electric fields may be obtained, and it is not difficult to make the light pass either normal or parallel to the electric field.

In describing portions of the spectrum, red will be considered as extending from λ 9000 to λ 6500; orange from λ 6500 to λ 6000; yellow from λ 6000 to λ 5750; green from λ 5750 to λ 5000; blue from λ 5000 to λ 4500; indigo from λ 4500 to λ 4250; violet from λ 4250 to λ 4000, and the ultra-violet from λ 4000 to λ 1800. Rays of greater wave-length than λ 9000 will be in the infra-red. These rays include heat rays and "reststrahlen" and have been extended to a wave-length of about 0.1 mm. Hertzian waves have been explored from wave-lengths of many meters to that of about 6 mm., leaving thus but a small gap between electromagnetic waves produced by ordinary mechanical devices and waves produced apparently by molecular aggregates. Waves of shorter wave-length than λ 1800 will be designated as Schumann waves.

CHAPTER III.

POTASSIUM SALTS.

Potassium chromate.—Potassium dichromate.—Potassium ferrocyanide.—Potassium ferricyanide.

Most potassium salts in solution are colorless, and for this reason it is considered that the potassium atoms do not themselves absorb any light in the visible portion of the spectrum. Several colored potassium salts are known and the colors of these are due in some way to the other atoms in the salt molecules. In the present work the absorption spectra of potassium ferricyanide, potassium ferrocyanide, potassium chromate, and potassium dichromate have been studied.

Using a 3-mm. length of solution of potassium ferricyanide in water we find that for a normal concentration there is complete absorption of all the shorter wave-lengths of light beyond λ 4800. As the concentration is decreased the edge of transmission moves continually towards the violet. It should be noticed that the region between complete absorption and complete transmission for the more concentrated solutions is quite narrow, being less than 40 Ångström units; solutions of this salt being thus quite good screens for absorbing light. Continually decreasing the concentration we reach a 0.0156 normal solution, when a transmission band begins to appear. For a certain range of concentration there appears an absorption band in the region λ 4200. Further decrease in concentration results in increasing transmission throughout the violet and ultra-violet. For dilutions greater than 0.00195 normal there is almost complete transmission throughout the ultra-violet. Very faint bands appear in the regions λλ 2500 to 2600, λλ 2950 to 3050 and λλ 3200 to 3250.

Several spectrograms were made of solutions for which the product of concentration and depth of layer were kept constant. In this case the spectrograms will be identical if Beer's law holds. According to this method of testing, Beer's law was found to hold within the ranges of concentration over which the spectrum was mapped.

The absorption of aqueous solutions of potassium ferrocyanide was investigated in the same way. A half-normal solution 3 mm. deep shows that all light of wave-lengths shorter than λ 3950 is absorbed. Keeping the depth of layer the same, it is found that with decrease in concentration the transmission gradually moves towards the ultra-violet, and for dilutions greater than 0.0078 normal there is transmission throughout the whole spectrum. Beer's law was found to hold.

A 2 normal aqueous solution of potassium chromate 3 mm. in thickness shows complete transmission of wave-lengths greater than λ 4950. Decreasing the concentration causes the transmission to move gradually towards the violet, and for a 0.01 normal solution a transmission band appears at λ 3100, or, in other words, there appears an absorption band whose center is about λ 3700. As the concentration decreases this absorption band fills up, the violet edge of the transmission band gradually pushes out into the ultra-violet, and for dilutions greater than 0.0005 normal there is complete transmission throughout the spectrum. Beer's law was found to hold for potassium chromate throughout the above ranges of concentration, except in the more concentrated solutions between 2 normal and 0.25 normal.

Potassium dichromate in water was found to have a much greater absorbing power than the solutions previously described. A one-third normal solution absorbed all wave-lengths shorter than λ 5350. As the concentration is decreased the transmission extends farther and farther out into the violet. For a 0.0026 normal concentration a transmission band appears in the violet, thus giving an absorption band whose center is about λ 3800. As the concentration is further decreased transmission becomes greater and greater in the violet and ultra-violet, and is practically complete for a 0.0006 normal concentration. Beer's law has been tested between the above ranges of concentration and has been found to hold.

In photometric measurements to test Beer's law, the equation defining the quantities to be measured is

$$J = J_0\, 10^{-Acl}$$

where J_0 is the intensity of the light that enters the solution (neglecting any loss due to reflection), J the intensity of the light as it leaves the solution, c the concentration in gram molecules of the salt per liter of solution, l the thickness of layer and A a constant if Beer's law holds. Strictly speaking, the above equation holds for monochromatic light. For ordinary white light we would have to integrate this equation over the range of wave-lengths used. The equation would then have the form

$$J = J_0 \int_{\lambda_1}^{\lambda_2} e^{\beta lc} d^{\lambda}$$

The quantity β is called the index of absorption and A the molecular extinction coefficient. If the absorption is proportionately greater in the more concentrated solutions, then Beer's law fails and A decreases inversely as the concentration.

λ	Potassium dichromate.	
	Value of A. $c=0.034$.	Value of A. $c=0.0034$.
509	62.4	58.0
521	28.7	26.2
536	7.24	6.2

From photometric measurements Settegast[1] and Sabatier[2] conclude that the absorption spectrum of potassium dichromate is the same as that of chromic acid, and that the absorption spectrum of potassium chromate is entirely different. This is corroborated by the present work. Settegast finds that Beer's law does not hold for potassium chromate and potassium dichromate, the coefficient A decreasing with increasing concentration. Grünbaum[3] finds the accompanying values of A and ε where $\varepsilon = c/A$.

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[1] Wied. Ann., **7**, 242–271 (1879).
[2] Compt. rend., **103**, 49–52 (1886).
[3] Ann. Phys., **12**, 1004, 1011 (1903).

It will be seen that the deviation here from Beer's law is in the opposite direction from that found by Settegast. Grünbaum finds that ε and therefore A depend on the depth of layer.

An example will be given where the same concentration and different depths of the solution were used:

λ.	Value of ϵ for $c=0.0034$.		
	25 cm. layer.	12 cm. layer.	5 cm. layer.
521	0.0758	0.0818	0.0884
521	.0761	.0830	.0897

Our work indicates that Beer's law holds for all dilute solutions, and usually the deviations for concentrated solutions are very small. Of the potassium salts above described, only potassium chromate between 2 normal and 0.25 normal showed any considerable deviation from Beer's law, and in this case the absorption of the concentrated solution was greater by about 40 Ångström units than would be expected if Beer's law held.

The present method is a very good qualitative test of Beer's law, and gives the results for each wave-length, whereas most photometric methods only give integrated results over a more or less wide region of wave-length. A very good review of the work upon Beer's law has been published by G. Rudorf.[1] A more detailed account of the work upon the potassium salts will now be given.

POTASSIUM CHROMATE.

Potassium chromate (K_2CrO_4) (Plates 1 and 2) was mapped for ranges of concentration between 2 normal and 0.00049 normal concentration. In every case the length of exposure to the Nernst glower was $\begin{Bmatrix}90\\80\end{Bmatrix}$ seconds, the current being 0.8 ampere, and when there was transmission in the ultra-violet, the length of exposure to the spark was 2 minutes. The slit-width was 0.08 mm. and the depth of cell in each case was 3 mm. The following table gives the limits of absorption bands. The limit is usually taken as midway between complete transmission and complete absorption. For the more concentrated solutions the region between complete absorption and transmission was quite narrow, not being more than 20 or 30 Ångström units. For the more dilute solutions the edges of the bands were much more diffuse.

This work here also (Plates 3 and 4) indicates that Beer's law holds for all dilute solutions which have thus far been tested, and usually the deviations from Beer's law for concentrated solutions is small. The present method is very crude as far as dealing with relative intensities. In some cases, however, it is quite sensitive, although it never gives absolute values for A. As an example, we will take that of potassium chromate between concentrations 2 normal and 0.25 normal. When the depth of cell is kept constant at 3 mm., the position of the edge of transmission for the 2 normal solution is $\lambda\,4970$, for the 0.25 normal solution $\lambda\,4750$. In the run for Beer's law (where cl is kept constant) it is found that the absorption is about 40

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[1] Jahrb. Rad. u. Elek., **3**, 422 (1906); and **4**, 380 (1907).

Ångström units nearer the violet for the most concentrated solution, compared with the 0.025 normal solution. This would mean that the value of *A* had increased with increase in concentration. On account of the sharpness of the edge of absorption it is possible to detect a change in the edge of 10 Ångström units, and this would correspond to a change in *A* of about 20 per cent. One of the larger errors entering into the determination is getting the depth of layer correct for their smallest values. The method is very useful in showing the results over the whole spectrum.

Concentration.	Edge of short wave-length absorption.	Edges of violet transmission band.		Concentration.	Edge of violet transmission band.
0.00049	λ 3820	λ 3600	....	0.03125	λ 4500
.00065	λ 3870	λ 3500	λ 2700	.042	λ 4520
.0009	λ 3900	λ 3450	λ 2800	.058	λ 4570
.0013	λ 3970	λ 3400	λ 2900	.083	λ 4640
.0019	λ 4000	λ 3350	λ 2940	.125	λ 4720
.0029	λ 4050	λ 3300	λ 2960	.19	λ 4750
.0039	λ 4100	λ 3240	λ 3000	.25	λ 4800
.0052	λ 4200	λ 3180	λ 3040	.33	λ 4840
.007	λ 4250	λ 3150	λ 3070	.47	λ 4880
.0104	λ 4350	λ 3140	λ 3100	.66	λ 4920
.015	λ 4400	....	....	1.0	λ 4960
.024	λ 4450	....	....	1.5	λ 4970
.03125	λ 4500	....	....	2.0	....

Potassium Dichromate.

The spectrograms showing the variation of absorption of potassium dichromate in water, keeping the depth of layer constant and changing the concentration, are Plate 5, *B*, and Plate 6, *A*, *B*. The absorption is much greater than for potassium chromate and the limits of the bands are much more diffuse. The change of the absorption with change in concentration is much greater than for potassium chromate.

The concentrations for *B*, Plate 5 are, beginning with the strip next to the scale, 0.333, 0.25, 0.16, 0.11, 0.083, 0.055, and 0.042 normal; the depth of layer being 3 mm. The distance between complete absorption and complete transmission is about 70 Ångström units for the 0.3 normal solution and over 200 Ångström units for the 0.04 normal solution. The limits of the absorption band beginning with the most concentrated solution are λλ 5340, 5320, 5300, 5240, 5200, 5140, and 5100.

For Plate 6, *A*, the concentrations are 0.042, 0.031, 0.021, 0.014, 0.0104, 0.0068, and 0.0052 normal, beginning with the strip next the scale. The depth of layer is 3 mm. In this case the edge of the absorption is very diffuse, the distance between complete absorption and transmission being over 200 Ångström units. The limits of the band for the various concentrations are λλ 5100, 4900, 4800, 4700, 4500, 4300, and 4200, approximately.

The concentrations for Plate 6, *B*, are 0.0052, 0.0039, 0.0026, 0.0017, 0.00087, and 0.00065 normal, starting with the strip nearest the scale. The limits of the red side of the absorption band are roughly λλ 4200, 4150, 4050, 4000, 3900. The violet edge of this absorption band makes its appearance at the concentration 0.0026 normal, and has a limit at about λ 3200. For 0.0017 normal the limit is 3300, and for 0.00087 normal, λ 3400. The middle of this absorption band for 0.00087 normal would thus be about λ 3800. The ultra-violet band which appears at 0.0017 normal has limits upon its red side of λ 3100; for 0.00087 normal, λ 3000; and 0.00065 normal, λ 2900.

Plate 5, *A*, tests Beer's law. Starting with the strip nearest the numbered scale the concentrations are 0.33, 0.25, 0.16, 0.11, 0.083, 0.055, and 0.042 normal; the corresponding depths of cell being 3, 4, 6, 9, 13, 18, and 24 mm. The limit of absorption is at λ 5350. Beer's law is found to hold.

Plate 7, *A*, and *B*, contains spectrograms in which Beer's law is tested for more dilute solutions. The concentrations and depths of cell are given in the general description of the plates. In *A* the limit of absorption is at λ 5000, in B at λ 4200. In both cases Beer's law holds. The edge of the absorption band in this case is quite broad.

Potassium Ferrocyanide in Water.

Potassium ferrocyanide has a color very similar to that of potassium ferricyanide. It is practically insoluble in all solvents except water. Its spectrum has been mapped out for concentrations ranging from 0.5 to 0.00078 normal, and Beer's law has also been tested between these limits.

The methods of exposure have been the same in all the spectrograms taken of the potassium salts. The time of exposure to the Nernst glower was 80 seconds, the current being 0.8 ampere and the slit width 0.08 mm. When there was any transmission in the ultra-violet, exposure was made for 120 seconds to the spark.

The mapping of the spectrum was done by keeping the depth of cell constant at 3 mm. and gradually changing the concentration of the solution. Plate 8, *A* and *B*, shows the variation of the absorption of light with variation in the concentration. Starting with the strip at the top of *A*, the concentrations were 0.5, 0.375, 0.25, 0.17, 0.117, 0.083, and 0.062 normal. The corresponding limits of absorption were λλ 3950. 3920, 3890, 3840, 3790, 3750, and 3700. The region between complete transmission and complete absorption was quite wide, being almost 100 Ångström units. This is in marked contrast with the sharp edge of the absorption band for concentrated solutions of potassium ferricyanide.

Starting with the upper strip of spectrogram *B*, the concentrations were 0.0625, 0.0469, 0.0312, 0.0208, 0.0144, 0.0103, and 0.0078 normal.

The corresponding limits of absorption in this case were λλ 3700, 3640, 3600, 3500, 3400, 3300 and 3150. For dilutions greater than this there is almost complete transmission throughout the whole violet region.

Two spectrograms (Plate 9, *A* and *B*) are given to show that Beer's law holds for solution of potassium ferrocyanide. Starting with the upper strip of *A*, the concentrations were 0.5, 0.375, 0.25, 0.17, 0.117, 0.083, and 0.062 normal. The corresponding concentrations in spectrogram *B* were 0.0625, 0.0469, 0.0312, 0.021, 0.0144, 0.0103, and 0.0078 normal. The depths of layer starting at the top of either *A* or *B* were 3, 4, 6, 9, 13, 18, and 24 mm. From the spectrograms we see that Beer's law holds within the range of concentrations studied.

The above spectrograms show that the absorption spectra of potassium ferricyanide and of potassium ferrocyanide are quite different. This difference is shown in three ways: First, for the same concentrations the absorption of potassium ferricyanide is much the greater; second, the limit of the absorption band of the ferricyanide is much sharper; and third, for certain concentrations of the potassium ferricyanide solution, there appears a blue-violet band having its center at about λ 4200. The band is entirely absent in the absorption of potassium ferrocyanide.

POTASSIUM FERRICYANIDE IN WATER.

Potassium ferricyanide, $K_3Fe(CN)_6$, usually exists in the form of dark-red anhydrous monoclinic prisms. It dissolves in water, giving a yellowish solution, which on dilution becomes lemon-yellow in color. According to Locke and Edwards[1] an isomeric form of potassium ferricyanide exists as olive-colored crystals having the composition $K_3Fe(CN)_6,H_2O$.

Potassium ferricyanide is but slightly soluble in solvents other than water, and for this reason the present work was limited to aqueous solutions.

One reason for examining the absorption spectra of potassium ferricyanide and potassium ferrocyanide was to find a clue, if possible, to the manner in which these solutions dissociated in dilute aqueous solutions. Most physical chemical investigators have considered that these two salts dissociate according to the following equations:

$$K_3FeC_6N_6 \rightleftarrows \overset{+}{K}, \overset{+}{K}, \overset{+}{K}, \overline{\overline{\overline{FeC_6N_6}}} \quad \text{and}$$

$$K_4FeC_6N_6 \rightleftarrows \overset{+}{K}, \overset{+}{K}, \overset{+}{K}, \overset{+}{K}, \overline{\overline{\overline{\overline{FeC_6N_6}}}}$$

The absorption spectra of these two salts would then be due to one or more of the four kinds of absorbers, $K_3FeC_6N_6$, $\overline{\overline{\overline{FeC_6N_6}}}$, $K_4FeC_6N_6$, and $\overline{\overline{FeC_6N_6}}$, and it is quite probable that each one of these absorbers would give rise to a different absorption spectrum.

According to Jones and Getman, and Jones and Bassett (Hydrates in Aqueous Solution, p. 46, Carnegie Institution of Washington Publication No. 60), it is possible that the dissociation takes place in a different manner. They concluded from conductivity measurements that potassium ferricyanide and potassium ferrocyanide dissociate as follows:

$$K_3FeC_6N_6 \rightleftarrows \overset{+}{K}, \overset{-}{CN}, \overset{+}{K}, \overset{-}{CN}, \overset{+}{K}, \overline{FeC_4N_4} \quad \text{and}$$

$$K_4FeC_6N_6 \rightleftarrows \overset{+}{K}, \overset{-}{CN}, \overset{+}{K}, \overset{-}{CN}, \overset{+}{K}, \overset{-}{CN}, \overset{+}{K}, \overline{FeC_3N_3}$$

The absorbers in an aqueous solution in this case would include four groups, $K_3FeC_6N_6$, $\overline{FeC_4N_4}$, $K_4FeC_6N_6$, nd $\overline{FeC_3N_3}$. Thus, according to either theory we get four kinds of absorbers. If we found that we had four different kinds of absorbers in potassium ferricyanide and potassium ferrocyanide solutions and mapped these spectra, and if we knew the absorption

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[1] Amer. Chem. Journ., **21**, 193 (1899).

spectra of either $\overline{\overline{\overline{FeC_6N_6}}}$, $\overline{\overline{FeC_6N_6}}$, $\overline{FeC_4N_4}$, or $\overline{FeC_3N_3}$, then we could tell whether the salts dissociated according to the first or the second theory, or according to some other method. But as we have thus far investigated only the absorption spectra of potassium ferricyanide and potassium ferrocyanide, no conclusion as to the manner of dissociation could be drawn.

It would be interesting in this connection to study potassium ferrocyanide carbonyl, $K_3FeC_5N_5CO:3\frac{1}{2}H_2O$, ferrocyanhydric acid, $H_4FeC_6N_6$, and ferricyanhydric acid, $H_3FeC_3N_3$. Both ferrocyanhydric acid and ferricyanhydric acid are soluble in water and alcohol.

The absorption spectra of a 3-mm. depth of cell of potassium ferricyanide in water were photographed between concentrations 1 normal and 0.00024 normal, and are given in Plates 10 and 11. The conditions of exposure in these two plates were the same, 80 seconds to the Nernst glower for the visible portion of the spectrum and 2 minutes to the spark for the ultra-violet region. The current through the Nernst glower was kept constant at 0.8 ampere. The slit-width was 0.08 mm.

Potassium ferricyanide has a very simple absorption spectrum. For the concentrated solutions all the short wave-lengths beyond the green are absorbed. As the concentration is decreased the limit of absorption gradually recedes towards the ultra-violet. The region between complete transmission and complete absorption is quite narrow for the more concentrated solutions, and for this reason solutions of potassium ferricyanide could be used as light-screens. The concentrations starting at the top of *A*, Plate 10 are 1, 0.75, 0.50, 0.333, 0.231, 0.166, and 0.125 normal, the corresponding limits of absorption being $\lambda\lambda$ 4800, 4780, 4765, 4730, 4710, 4680, and 4650. The distance between complete absorption and complete transmission as measured on the spectrum photograph was not greater than 40 Ångström units.

The concentrations starting at the top of *B*, Plate 10 are 0.125, 0.0937, 0.0625, 0.0417, 0.029, 0.0208, and 0.0156 normal. The corresponding limits of absorption are $\lambda\lambda$ 4650, 4630, 4620, 4600, 4560, 4520, and 4500. As the concentration becomes small the limit of absorption becomes more and more diffuse. For the 0.0156 normal concentration the distance between complete transmission and complete absorption was almost 100 Ångström units. For about this concentration a faint transmission band begins to appear in the ultra-violet.

The concentrations starting at the top of *A*, Plate 11 are 0.0156, 0.0117, 0.0078, 0.0052, 0.0036, 0.0026, and 0.00195 normal. In this spectrogram two bands of absorption appear, a blue-violet band and an ultra-violet band. For the 0.0156 normal solution the blue-violet absorption band is bounded by λ 4500 and λ 3570, for 0.0117 normal by $\lambda\lambda$ 4450 and 3580, for 0.0078 normal $\lambda\lambda$ 4400 and 4000. The middle of the band at its origin is about λ 4200. The long wave-length edge of the ultra-violet band has the following positions, for normal 0.0156, λ 3550; 0.0117, λ 3500; 0.0078, λ 3300; 0.0052, λ 3250; and 0.0036, λ 3150. For concentrations less than this there is more or less general transmission throughout the ultra-violet region.

The concentrations for *B*, Plate 11, starting with the strip nearest the top, were 0.00195, 0.00146, 0.00098, 0.00065, 0.00045, 0.00037, and 0.000244 normal. In this spectrogram there is somewhat general transmission throughout the whole ultra-violet region. In the ultra-violet there appear three weak bands that do not seem to be due to any feeble intensity of the spark-spectra in these regions. The positions of these bands are λ 2500 to 2600, λ 2950 to 3050, and λ 3200 to 3250.

Spectrograms were made to test Beer's law between concentrations 1 and 0.000244 normal, four spectrograms being made in all. In each one of these spectrograms the amount of absorbing salt in the solution through which the light passed, times the length of the solution was constant. Under these conditions if Beer's law holds the absorption spectra in each strip will be the same.

Plate 12, *A* represents a spectrogram showing that Beer's law holds for a potassium ferricyanide solution between concentrations 1 and 0.125 normal. Starting with the strip at the top the concentrations were 1, 0.75, 0.50, 0.333, 0.231, 0.166, and 0.125 normal. The depths of cell were 3, 4, 6, 9, 13, 18, and 24 mm., respectively. The exposure to the Nernst glower was made for 80 seconds, slit-width being 0.08 mm. and the current 0.8 ampere. The limit of absorption for each strip is λ 4800. *B*, Plate 12, was taken under the same conditions as *A*, each strip, however, being exposed to the spark for 3 minutes. The concentrations for *B*, starting with the upper strip, were 0.125, 0.094, 0.0625, 0.0417, 0.029, 0.0208, and 0.0156 normal, the depths of cell being 3, 4, 6, 9, 13, 18, and 24 mm. In this case also Beer's law held to within the limits of error of this method.

Spectrograms not published were made in a similar way for concentrations 0.0156, 0.0117, 0.0078, 0.0052, 0.0036, 0.0026, and 0.00195 normal; also for concentrations 0.00195, 0.00146, 0.00098, 0.00065, 0.00045, 0.00037, and 0.000244 normal, the depths of cell being 3, 4, 6, 9, 13, 18, and 24 mm., respectively. In all these cases Beer's law holds.

A question that is sometimes asked is, What is the sensitiveness of this method to small changes in concentration? This depends of course on the absolute concentration itself. For concentrated solutions of potassium ferricyanide it is possible to detect a change in the edge of the absorption to within 10 Ångström units. For concentrations of 0.125 normal, then, it would be possible to detect changes of concentration of less than normal 0.02. It will be noticed that the relative sensibility to change in concentration is not very great, but for dilute solutions the absolute sensibility is much greater. One reason for this is that errors in the depth of cell for a considerable cell-depth are small as compared with the depth of cell itself.

CHAPTER IV.

COBALT SALTS.

Review of previous work.—Cobalt chloride and bromide in glycerol.—Effect of rise in temperature on aqueous solutions of cobalt chloride, cobalt nitrate, cobalt sulphate, cobalt acetate, and cobalt sulphocyanate.—Effect of rise in temperature on the absorption spectra of aqueous solutions of mixtures of cobalt chloride and aluminium chloride, and of cobalt chloride and calcium chloride. Conductivity data.—Summary.

REVIEW OF PREVIOUS WORK.

Some of the most beautiful color-changes known are those shown by solutions of cobalt and copper salts. For example, aqueous solutions of cobalt chloride are purplish red in color. When a concentrated aqueous solution of cobalt chloride is heated, or treated with hydrochloric acid, aluminium chloride, or calcium chloride, its color changes to blue, the change being quite sudden under certain conditions. On the other hand, the addition of zinc and mercury chlorides produces the reverse effect, changing the blue solution into a red one. Similar changes result when cobalt salts dissolved in other solvents are treated in the same way as aqueous solutions. A very considerable amount of work has been done by various workers and in general different theories have been offered to explain the results.

Russel,[1] Potilitzin,[2] Lescoeur,[3] Etard,[4] and others favored the view that these color-changes were due to the formation of different compounds of the cobalt salt with the solvent. The hexahydrate $CoCl_2.6H_2O$ is red, and when heated it is changed into the reddish lilac dihydrate $CoCl_2.2H_2O$. When the latter compound is heated it is transformed into the dark-violet monohydrate, $CoCl_2.H_2O$. The anhydrous salt is blue and is formed at about 140° C. Etard showed that the solubility curve changed in direction at the same temperature that the red solution becomes blue. Charpy[5] showed the same to be true for the vapor-tension temperature curve.

Engel,[6] Donnan and Bassett,[7] Donnan,[8] Moore,[9] and others do not believe that these color-changes are solvation effects at all. Engel considers that double haloid salts may be formed. He points out the fact that the blue anhydrous cobalt chloride becomes red when sufficiently cooled, and that the red anhydrous sulphate becomes violet when heated. Donnan and Bassett consider that the blue color of cobalt salts is due to the formation of complex anions containing cobalt. By boiling-point determinations

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[1] Proc. Roy. Soc., **32**, 258 (1881); Chem. News, **59**, 93 (1889).
[2] Bull. Soc. Chem. (3), **6**, 264 (1891); Ber. d. deutsch. chem. Gesell., **17**, 276 (1884).
[3] Ann. Chim. Phys. (6), **19**, 547 (1890).
[4] Compt. rend., **113**, 699 (1891).
[5] *Ibid.*, **113**, 794 (1901).
[6] Bull. Soc. Chim. (3), **5**, 460 (1901).
[7] Journ. Chem. Soc., **81**, 942 (1902).
[8] Versuche über der Beziehung zwischen der elektrolytischen Dissoziation und der Lichtabsorption in Lösungen. Zeit. phys. Chem., **19**, 465–488 (1896); **53**, 317–320 (1905).
[9] Phys. Rev., **23**, No. 4, p. 321, 357 (1906).

they concluded that mercuric and cobalt chlorides in solution form compounds. When metallic ions of relatively strong basic properties like the alkaline earths or hydrogen are introduced with chlorine ions into a cobalt chloride solution, there is a greater formation of complex cobalt anions similar to that given by the following equation.

$$CoCl_2+2\overline{Cl} \rightleftarrows \overline{Co}\overline{Cl}_4 \qquad CoCl_2+\overline{Cl} \rightleftarrows \overline{CoCl}_3$$

On the other hand, Zn, Cd, Hg, Sb, Sn, etc., form negative complexes easier than cobalt and hence they will cause the cobalt complexes to break up.

$$\overline{Co}\overline{Cl}_4 \rightleftarrows CoCl_2+2\overline{Cl} \qquad ZnCl_2+2Cl \rightleftarrows \overline{Zn}\overline{Cl}_4$$

Vaillant[1] has made a quantitative comparison between dissociation and light absorption. In general there is a close parallelism between these two phenomena. For concentrated solutions, however, there are marked differences which suggest other products, and these Vaillant called hydrates. Pflüger,[2] Vaillant and Moore[3] have studied various salt solutions photometrically. They find the same absorption coefficients for dilute solutions of sodium, potassium, and barium permanganates, but for concentrated solutions they find differences. They conclude that absorption depends upon ionization.

A very detailed study has been made by Hartley[4] of the effect of temperature on the absorption spectra of solutions. Hartley considered that the effect of change in temperature was largely due to change in the solvation of the dissolved salt. Bois and Elias[5] studied cobaltammoniumrhodamid at 18° and −190° C. At the lower temperature the bands were smaller but were still very diffuse.

Uhler[6] has studied cobalt salts very systematically. Cobalt chloride in water was found to show rather fine bands at λ 6970, λ 6610, λ 6400 (weak), λ 6245 (weak), and λ 6095 (weak). In ethyl alcohol bands were found at λ 6950, λ 6360, λ 6150, and λ 6000.

Jones and Anderson[7] have made a detailed study of cobalt salts. Solutions of all the salts studied, except the sulphate, have a region of ultraviolet one-sided absorption. This they consider as due to association or solvation. In addition to the one-sided ultra-violet band, cobalt chloride has a band at λ 3300 which disappears very rapidly with dilution. This band they believe is due to some simple hydrate, and they consider that this simple hydrate is only stable in very concentrated solutions or at high temperatures. The green band appears for all aqueous solutions, and is independent of whether the cobalt exists as an ion, molecule, as an aggregate, or as a solvate; the absorbing power being apparently due to the cobalt

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[1] Ann. Chim. Phys. (7), **28**, 213 (1903).
[2] Ann. Phys. (4), **12**, 1903.
[3] Loc. cit.
[4] Dub. Trans. (2), **7**, 253, 312 (1900).

atom. Absorption in the red is considered to be due to a simple solvate. In alcohol cobalt chloride has bands at λ 3100 and λ 3600, and also a green band. In methyl alcohol they find a fairly narrow band at λ 5910, one at λ 6050; a narrow intense band at λ 6240; a wide band at λ 6450, and a wide intense band at λ 6700. The position and relative intensity of these bands are very different from that of the cobalt chloride water-bands described by Uhler. In acetone broad bands appear at λ 5725, λ 6200, and λ 6780. These do not appear to be broken up into sharper bands under any conditions. By the addition of 5 per cent of water to an ethyl alcohol solution of cobalt chloride, the water-bands are made to appear, while for an acetone solution it requires the presence of at least 10 per cent of water to bring out the water-bands. Cobalt and calcium bromides in water are found to give bands at λ 6400, λ 6650, and λ 6950. Cobalt bromide in acetone has bands in the red that differ quite markedly from those of cobalt chloride in acetone.

Cobalt chloride in water (Böhlendorf).	$CoCl_2$ in alcohol (Böhlendorf).	Cobalt chlorate in alcohol (Formánek).
λ 7100 to 6880	λ 7100 to 6570	λ 6850 to 6320
λ 6750 to 6530	....	....
λ 6400	λ 6400	....
λ 6260 to 6170	λ 6250 to 6170	λ 6245
λ 6070	λ 6070	λ 6058
λ 5610 to 4980	....	λ 5906
		λ 5720
		λ 5265
		λ 5120

Rizzo[1] has investigated the effect of rise in temperature on the absorption bands of cobalt glass. He gives the following figures:

15°.	300°.	500°.
λ 6870 to λ 6380	λ 6900 to λ 6480	λ 6920 to λ 6460
λ 6030 to λ 5780	λ 6110 to λ 5800	λ 6130 to λ 5800
λ 5520	λ 5630	λ 5650

From the above summary it will be seen that our knowledge of the red cobalt bands is very small at present. Much more work, similar to that to be described on the uranyl bands, remains to be done. Apparently these cobalt bands are somewhat different from the uranyl bands; at any rate, the bands investigated by Bois and Elias did not break up into fine, sharp bands at very low temperatures.

In discussing the various spectrograms that show the effect of change in temperature on the absorption spectra of salts, these spectra will be divided into three kinds:

The first kind of absorption consists of wide bands, in many cases hundreds of Ångström units wide. In many of the spectrograms only one edge of the band may appear, the other edge of it lying in parts of the spectroscopic apparatus is not properly adapted. Examples of this kind of absorption are given by the copper or nickel salts, the ferricyanides, the chromates, etc. There is not the slightest indication of a finer structure to these bands.

The second kind of absorption spectra consists of diffuse bands that are quite narrow in many cases and are usually very weak at ordinary temperatures. These bands may be from 10 to several hundred Ångström units wide, and at very low temperatures may be broken up into finer and sharper bands. Examples of this kind of bands are the cobalt, uranyl, or uranous bands. In many cases these bands appear only under very special conditions of concentration and depth of cell. If the amount of absorbing material is large there is usually a wide absorption band in the region. This is well illustrated by the uranyl bands and the blue-violet band of the uranyl salts. If the amount of absorbing material is small the transmission of light is so great that these faint bands are entirely obliterated.

The third class of bands are sharp and appear over rather wide ranges of concentration. They are exemplified by the neodymium and erbium bands. This classification of bands is quite adequate for the present article on account of the salts studied and the temperatures used. It is very probable, however, that the latter two kinds of bands gradually merge into each other.

Glycerol Solutions of Cobalt Salts.

A dilute solution of cobalt chloride was placed in the silica cell and exposures were made at 10°, 100°, and 200° C. At 10° and 100° there was practically complete transmission throughout the visible portion of the spectrum. At 200° the whole shorter wave-length portion of the spectrum was absorbed up to λ 6200. No indications of any fine bands in the red were to be noticed. A solution of normal cobalt bromide in glycerol was exposed in the same way as the chloride, with practically no change in the absorption with rise in temperature. A more concentrated solution of cobalt bromide in glycerol was exposed in the silica cell at 10°, 100°, and 200°. At 10° there was a very diffuse absorption band extending from λ 5000 to λ 5300. At 100° this band had broadened so as to reach from λ 4900 to λ 5400. At 200° the whole of the spectrum of wave-length less than λ 6200 was absorbed. No signs of the red bands appeared. Concentrated solutions of cobalt salts in glycerol become blue on being heated. Unfortunately the length of the silica cell prevented the use of concentrated solutions.

Aqueous Solutions of Cobalt Salts.

A spectrogram, Plate 13, *A*, of the absorption spectrum of an aqueous solution of cobalt chloride was made for a 2.37 normal concentration and a depth of cell of 1.3 mm. The current in the Nernst glower was 0.7 ampere, slit-width 0.20 mm. and the time of exposure 3 minutes. No exposure was made to the spark in this instance. The temperatures were 2°, 14°, 30°, 45°, 60°, 70°, and 81° C.

At the lowest temperature there is an absorption band extending from λ 4800 to λ 5100. As the temperature rises this band broadens, the broadening being quite slow at first. At 60° the limits of the band are λ 4700 to λ 5600. At the higher temperatures the increase in the absorption throughout the red becomes very great, and at 81° the absorption is practically complete. It is for this reason that the cobalt chloride solution becomes blue. Bands appear at λ 6310 and λ 6440 at 72° and 81°.

Plate 13, *B*, gives the absorption spectra of a 0.315 normal concentration and a depth of layer of 10 mm. This solution does not change in color and shows only an increased widening of the bands. The intense absorption in the red does not take place under these conditions of concentration and temperature.

A spectrogram showing the effect of rise in temperature was made for an aqueous solution of cobalt chloride, using a 2.37 normal solution, and a depth of cell of 3 mm. The length of exposure to the Nernst glower was 2 minutes, using 0.8 ampere current and a slit-width of 0.20 mm. The length of time of exposure to the spark was 5 minutes. Starting from the numbered scale the temperatures were 0°, 14°, 28°, 44°, 58°, and 73°.

The region of the spectrum beyond λ 3000 is absorbed. The amount of this absorption does not vary for the above changes in temperature. Throughout the ultra-violet region of the spectrum there is a very considerable amount of general absorption of light. At 0° there is a wide absorption band between λ 4500 and λ 5900. The ultra-violet edge of this band is not affected by change in temperature; the edge in the yellow, however, widens out towards the longer wave-lengths with rise in temperature. The boundaries of this edge are λ 5900 at 0°, λ 5950 at 14°, λ 6000 at 28°, λ 6050 at 44°, and λ 6100 at 58°. Above 60° there is very little transmission in the red end of the spectrum.

At the higher temperatures as the transmission in the red is greatly decreased, several cobalt bands appear. The bands at λλ 6300 and 6450 are of about equal intensity and about 40 Ångström units wide. A very faint band appears at about λ 6620.

The Wratten and Wainwright films are sensitive to approximately λ 7200 on short exposures. At 0° cobalt chloride allows light to pass with as long wave-lengths as can record themselves on the films. At the higher temperatures, however, this is not the case. At 44° the light beyond λ 7000 is absorbed, and at 60° all light beyond λ 6800.

A spectrogram showing the effect of rise in temperature was made for an aqueous solution of cobalt chloride of 2.37 normal concentration and 1 mm. depth of cell. The length of exposure to the Nernst glower was 3 minutes, current 0.7 ampere, slit-width 0.20 mm. The exposure to the spark was for 3 minutes. Starting with the solution next to the numbered scale, the temperatures were 1°, 12°, 27°, 45°, 60°, 70°, and 85°.

The spectrum in the ultra-violet beyond λ 3000 was completely absorbed by the cobalt chloride. The whole region between λ 3000 and λ 5000 is a region of considerable absorption, possibly half of the light being transmitted. Between λ 5000 and λ 5600 there is an absorption band with diffuse edges. This absorption gradually widens with rise in temperature until at 85° it extends from λ 5000 to λ 5800; the widening being slightly unsymmetrical.

The cobalt bands λλ 6315 and 6440 appear in the spectrum strip taken at 85°. At this temperature there is a very large amount of general absorption from λ 5800 on to λ 6800. Beyond λ 6800 the absorption is complete. The faint band at λ 6620 also appears at this temperature. The bands λλ 6315 and 6440 appear at lower temperatures, but the transmission is so great for the long exposures necessary for the other regions of the spectrum that the bands are almost obliterated.

A spectrogram (Plate 15, *A*) showing the effect of rise in temperature was made for an aqueous solution of cobalt chloride 0.125 normal concentration and a layer 12 mm. long. Exposures of 4 minutes were made to the Nernst glower, current 0.8 ampere, slit-width 0.20 mm. The time of exposure to the spark was 6 minutes. Starting with the strip next to the numbered scale, the temperatures were 5°, 18°, 38°, 52°, 64°, and 83°.

The absorption spectrum of cobalt is characterized by two wide bands in the visible spectrum and an ultra-violet band. At 5° the ultra-violet band extends to λ 2700. As the temperature rises this band widens slightly, its edge falling at about λ 2800 at 83°. The edge of this absorption band is quite sharp. The violet band extends from about λ 4000 to λ 4400 at 5°. This band is very diffuse, there being considerable transmission throughout the whole extent of the band. The yellow band extends from λ 5500 to λ 6100 at 5°, there being slight general transmission also throughout the whole extent of this band. Both these bands gradually broaden with rise in temperature, and at 83° the limits of the violet band are λλ 4000 and 4600; of the yellow band λλ 5500 and 6400. It will be seen that these bands widen unsymmetrically, the short wave-length edges remaining nearly stationary, while the long wave-length edges recede towards the red. The amount of transmitted light in the red region from λ 6400 to λ 7000 is much less at the higher temperatures.

A spectrogram (Plate 13, *B*) was made of an aqueous solution of cobalt chloride of 0.315 normal concentration and 10.4 mm. depth of cell. The exposures were 3 minutes to the Nernst glower; the current being 0.7 ampere and the slit-width 0.20 mm. Starting with the strip adjacent to the comparison scale, the temperatures were 2°, 14°, 30°, 44°, 60°, 75°, and 81°.

The most noticeable effect of rise in temperature on the absorption spectra of cobalt chloride is to widen the band in the green. At 1° this band extended from λ 4900 to λ 5300, at 45° from λ 4800 to λ 5400. Above this temperature the band widens quite rapidly, and at 83° it extends from λ 4500 to λ 5700. The widening is approximately symmetrical.

A spectrogram similar to the one described above was made with a cobalt chloride solution of 0.315 normal concentration and a depth of layer of 24 mm. No exposure was made to the spark at all. At the lowest temperature, 4°, the whole of the short wave-length spectrum was absorbed up to λ 5700. No trace of the cobalt bands in the red was noticeable.

A spectrogram was made to compare with the one described immediately above. These two spectrograms were taken under the same conditions, and with the same amount of cobalt chloride in the path of the beam of light. In the solution used for the spectrogram now being described, the concentration was 2.52 normal and the length of cell 3 mm.

At the lower temperatures the effect of rise in temperature was the same for both solutions. In the case of the concentrated solution all light was practically absorbed at 70°, a narrow transmission band in the blue being the only light not absorbed. At about 50° the bands in the red appear. Their wave-lengths are approximately $\lambda\lambda$ 6100 and 6250.

A spectrogram was made of a 2.52 normal concentration of cobalt chloride in water and having a depth of cell of 1.3 mm. This spectrogram showed an extremely diffuse band between about λ 4600 and λ 5500. Rise in temperature had very little effect on absorption, except in the red region, where the general absorption was greatly increased. At 38° the cobalt bands appear and increase in intensity with rise in temperature. Their positions are about $\lambda\lambda$ 6100 and 6250—the same positions as on the previous plate.

A spectrogram (Plate 14, *A*) was made showing the effect of rise in temperature on a 0.0394 normal concentration of cobalt chloride in water. At 5° the cobalt band extended from λ 4400 to λ 5600. At 75° it had widened out to λ 4300 and λ 5750. For a dilute solution it will be seen that rise in temperature produces only a small change in the absorption spectra.

Cobalt Nitrate.

A spectrogram (Plate 14, *B*) was made showing the absorption spectra of a 2.3 normal aqueous solution of cobalt chloride of 2 mm. depth. The exposures to the Nernst glower were for 3 minutes, current 0.7 ampere and slit-width 0.20 mm. Starting with the strip adjacent to the numbered scale, the temperatures were 2°, 14°, 30°, 45°, 60°, 75°, and 85°.

The effect of rise in temperature on the absorption spectrum of cobalt nitrate was not great. The wide band in the yellow extended from λ 4600 to λ 5500 at 2°. The band gradually widened with rise in temperature, and at 85° extended from λ 4450 to approximately λ 5650.

It will be noticed that the effect of rise in temperature on the absorption spectra of cobalt nitrate is very small compared with that of cobalt chloride. Hartley considered that salts crystallizing with the largest amounts of water usually showed the greatest change in their absorption spectra when heated. These two cobalt salts, however, both crystallize from aqueous solutions with 6 molecules of water.

A spectrogram (Plate 15, *B*) was made of cobalt nitrate in water, of 0.287 normal concentration and a 3 mm. length of cell. The length of exposure to the Nernst glower was 2 minutes and to the spark 3 minutes. The current in the glower was 0.8 ampere and the slit-width 0.20 mm. The temperatures, starting with the strip nearest the comparison spectrum were 13°, 27°, 42°, 61°, 73°, and 85°.

At ordinary temperatures cobalt nitrate crystallizes out with 6 molecules of water. The effect of rise in temperature on the absorption spectra of cobalt nitrate at this concentration was very small. The NO_3 ultraviolet band extended to about λ 3300. It did not appear to be affected in the least by the change in temperature. A weak band from λ 5000 to λ 5200 appears at the higher temperatures, increasing in intensity slightly with rise in temperature.

Cobalt Sulphate.

A spectrogram (Plate 16, *A*) of the absorption spectra of a normal aqueous solution of cobalt sulphate was made for the different temperatures, 6°, 19°, 36°, 49°, 64°, and 80°; the strip representing the lowest temperature being nearest the comparison spectrum. The depth of cell was 3 mm., the length of exposure to the Nernst glower 2 minutes, to the spark 6 minutes. The current through the glower was 0.8 ampere and the slit-width 0.20 mm.

The absorption spectrum of cobalt sulphate under these conditions consists at 6° of a band in the yellow from λ 4900 to λ 5250. At 80° this band has widened almost symmetrically and extends from λ 4800 to λ 5400. Except the change in this band rise in temperature produced no appreciable effect.

Cobalt Acetate.

Two spectrograms were made of cobalt acetate in water; the first (Plate 17, *A*) being of normal concentration and 3 mm. depth of cell, and the second being 0.125 normal concentration and 24 mm. depth of cell. Starting with the strip nearest the comparison spectrum, the temperatures were 4°, 18°, 32°, 49°, 64°, and 79° for the concentrated solution, and 7°, 27°, 47°, 61°, 73°, and 81° for the more dilute solution. The time of exposure for each concentration was 6 minutes to the spark and 2 minutes to the Nernst glower, current being 0.8 ampere and slit-width 0.20 mm.

At the lowest temperature there was transmission in the ultra-violet out to λ 2400. This transmission decreased with rise in temperature, and at 80° extended to λ 2600 for both concentrations. For the yellow-green band, however, the effect of temperature was much greater in the case of the concentrated solution. For the more concentrated solution at 4° the yellow-green band extended from λ 4900 to λ 5400. As the temperature was raised it increased in width until at 64° it extended from λ 4600 to λ 5700. The widening produced by heating the solution to 79° from 64° is unsymmetrical, the band now extending from λ 4550 to λ 6000. For the dilute solution at 70° the yellow-green band extends from λ 4900 to λ 5300, and at 81° from approximately λ 4650 to λ 5600. This yellow-green band has very diffuse edges and there is usually a slight general transmission throughout the whole extent of the band.

Cobalt Chloride and Calcium Chloride.

A spectrogram (Plate 18, *A*) was made to show the effect of rise in temperature on a mixture of cobalt chloride and calcium chloride in water. The concentration of the cobalt chloride was 0.237 normal and of the calcium chloride 4.14 normal. The length of layer was 2 mm. The exposure to the Nernst glower was for 3 minutes; the current being 0.7 ampere and the slit-width 0.20 mm. The length of exposure to the spark was 3 minutes. Starting with the strip nearest the comparison scale, the temperatures were 2°, 15°, 30°, 42°, 60°, 75°, and 85°.

Throughout the whole ultra-violet region there was strong absorption, but this did not indicate the existence of any banded structure. The only portion of the spectrum showing any change due to temperature was at the red end of the spectrum. The increase of absorption in this region will be given for each temperature. At 2° there was transmission to λ 7100, below which the film was but slightly sensitive; at 15° the limit of transmission being λ 6900; at 30° λ 6700, while at the same time the cobalt bands appear; at 42° the whole region from λ 6050 to λ 6500 is very weak and shows the cobalt bands at λλ 6105, 6240, and 6415; at 60° the limit of transmission is at λ 6000; at 75° λ 5900, and at 85° λ 5800.

Cobalt Chloride and Aluminium Chloride.

A spectrogram (Plate 18, *B*) was made showing the effect of rise in temperature on the absorption spectra of an aqueous solution of 0.161 normal cobalt chloride and 2.75 normal aluminium chloride. The depth of layer was 2 mm. The length of exposure to the Nernst glower was 3 minutes, current 0.7 ampere, and slit-width 0.20 mm. Starting with the strip nearest the numbered scale, the temperatures were −1.5°, 13°, 31°, 45°, 60°, 72°, and 87°.

As no spark was used there is of course no impression on the photographic film in the ultra-violet. The only region of absorption is in the red and this increases very rapidly with rise in temperature. The cobalt bands appear at −1°. At −1° the transmission extends to λ 6900; at 13° to λ 6800; at 31° there is almost complete absorption to λ 6100. The cobalt bands do appear approximately at λλ 6100, 6150 and 6420; at 45° the absorption extends to λ 6050; at 60° to λ 5950; at 72° to λ 6900, and at 87° to λ 5850.

A spectrogram (Plate 19, *A*) was made to test the effect of rise in temperature on the change in the absorption spectra of a dilute solution of cobalt chloride (0.00316 normal) in a concentrated (3.06 normal) solution of aluminium chloride in water. The length of layer was 150 mm. The time of exposure was 2 minutes to the Nernst glower and 4 minutes to the spark. The current through the glower was 0.8 ampere and the slit-width 0.20 mm. Starting with the strip adjacent to the comparison scale, the temperatures were 1°, 18°, 41°, 55°, 68°, and 85°.

The effect of rise in temperature in this case was greater than in that of a more concentrated solution of cobalt chloride. There is absorption in the whole violet region, so that the spectrum at 1° consists simply of a transmission from λ 4000 to λ 6500. The transmission is weak from λ 6100 to λ 6500 and shows the cobalt bands at λλ 6100, 6350 (about 100 Ångström units wide), and 6420. At 18° the transmission band runs from λ 4000 to λ 6050. With rise in temperature the transmission band narrows and at 85° extends only from λ 4300 to λ 6750. Weak bands about 100 Ångström units wide appear at λλ 5050 and 5300. These are considerably broader at the lower temperatures.

A spectrogram (Plate 19, *B*) was made to show the effect of rise in temperature on the absorption spectra of a 0.0095 normal cobalt chloride and 4.6 normal calcium chloride solution in water. The depth of the layer was 50 mm., the length of exposure to the Nernst glower 3 minutes, the current 0.7 ampere and the slit-width 0.20 mm. The length of exposure to the spark was 5 minutes. The temperatures, starting with the strip adjacent to the comparison scale, were −1.5°, 20°, 30°, 45°, 57°, 74°, and 88°.

The ultra-violet absorption reached to about λ 3000, with a great deal of general absorption throughout the violet. This general absorption increased slightly with rise in temperature. At —1.5° there was transmission to λ 6900, and at 20° to λ 6800. At 20° and 30° the cobalt bands show quite strongly at λλ 6100, 6240, 6400. At 45° the absorption reaches to λ 6050, at 57° to λ 5950, at 74° to λ 5850, and at 88° to λ 5800.

Wide bands appear at approximately λ 5000 and λ 5300. These bands are very weak, considerably weaker than for a solution of cobalt chloride and aluminium chloride.

Cobalt Sulphocyanate.

A spectrogram (Plate 20, *A*) was made to show the effect of change in temperature on a 2-normal aqueous solution of cobalt sulphocyanate ($CoS_2C_2N_2$), 1 mm. deep. The length of exposure was 3 minutes to the Nernst glower, the current being 0.8 ampere and the slit-width 0.20 mm. The length of exposure to the spark was 6 minutes. Starting with the strip nearest the comparison scale, the temperatures were 3°, 18°, 31°, 45°, 59°, and 80°.

Under these conditions of concentration and depth of layer the cobalt sulphocyanate absorption consists of an ultra-violet absorption band and a wide band in the yellow and green. As the temperature is raised these bands both widen out on the red side. The effect of temperature is especially marked between 60° and 80°. The limits of the ultra-violet absorption are λ 3400 at 3°, λ 3450 at 18°, λ 3450 at 31°, λ 3500 at 45°, λ 3550 at 59°, and λ 3600 at 80°.

For the yellow-green band the limits are λ 4550 to λ 5600 at 3°, λ 4550 to λ 5630 at 18°, λ 4550 to λ 5650 at 31°, λ 4570 to λ 5700 at 45°, λ 4550 to λ 5750 at 59°, and λ 4550 to λ 6400 at 80°. At 59° there is a weak and broad band extending from λ 6000 to about λ 6300.

The remarkable feature of this spectrogram is that the yellow-green band widens only on the red side.

A spectrogram (Plate 20, *B*) was made of a much more dilute solution of cobalt sulphocyanate in water, the concentration being 0.25 normal and the depth of cell 8 mm. The time of exposure to the Nernst glower with a current of 0.8 ampere and a slit-width of 0.20 mm. was 2 minutes. The length of exposure to the spark was 6 minutes. Starting with the strip adjacent to the comparison spectrum, the temperatures were 6°, 20°, 33°, 47°, 59°, 73°, and 80°.

In this spectrogram the effect of temperature on the absorption spectra of cobalt sulphocyanate was very small as compared with the effect on the 2-normal solution. At 6° the ultra-violet band absorbed pretty completely up to λ 3220. There was a slight transmission of light where a strong spark-line was located, but this was small. The edge of the band was quite sharp. The yellow-green band extended from λ 4600 to λ 5500. At 80° the ultra-violet band has absorbed everything to λ 3300. The yellow-green band at this temperature runs from λ 4600 to λ 5600, showing a slight widening on the side of the longer wave-lengths.

Cobalt Chloride in Water; Conductivity and Dissociation.

The conductivities of solutions of cobalt chloride at the temperatures 35°, 50°, and 65° were determined, and the approximate dissociations at these temperatures calculated. The hydrolysis especially at the more elevated temperatures made it impossible to calculate the dissociations accurately. v is the volume, μv the molecular conductivity.

V.	35°.		50°.		65°.		Temperature coefficients.			
							35° to 50°.		50° to 65°.	
	μv	α	μv	α	μv	α	Cond. units.	Per cent.	Cond units.	Per cent.
4	188.3	66.1	226.4	61.4	274.3	59.2	2.54	1.35	3.19	1.41
8	197.6	69.3	249.4	67.6	302.5	65.3	3.45	1.74	3.54	1.42
32	227.7	79.9	288.7	78.3	355.6	76.8	4.07	1.79	4.46	1.54
128	255.1	89.5	326.7	88.6	404.2	87.3	4.77	1.87	5.17	1.58
512	275.5	96.6	352.2	95.5	442.8	95.6	5.11	1.86	6.04	1.71
1024	285.1	100.0	368.7	100.0	463.2	100.0	5.57	1.95	6.30	1.71

Cobalt Bromide in Water; Conductivity and Dissociation.

V.	35°.		50°.		65°.		Temperature coefficients.			
							35° to 50°.		50° to 65°.	
	μv	α	μv	α	μv	α	Cond. units.	Per cent.	Cond. units.	Per cent.
4	189.8	65.7	239.0	64.5	289.6	62.4	3.28	1.73	3.37	1.41
8	205.1	71.0	259.4	70.0	315.7	68.0	3.60	1.75	3.75	1.44
32	235.6	81.5	299.5	80.8	367.3	79.1	4.26	1.81	4.52	1.51
128	258.0	89.3	329.5	88.9	406.7	87.6	4.77	1.85	5.15	1.56
512	275.6	95.4	353.1	95.3	436.6	94.0	5.12	1.87	5.57	1.58
2048	289.0	100.0	370.6	100.0	464.3	100.0	5.44	1.88	6.25	1.68

Cobalt Nitrate in Water; Conductivity and Dissociation.

Cobalt nitrate, like cobalt chloride, is somewhat hydrolyzed in dilute solutions. The dissociations α are, therefore, only approximations.

V.	35°.		50°.		65°.		Temperature coefficients.			
							35° to 50°.		50° to 65°.	
	μv	α	μv	α	μv	α	Cond. units.	Per cent.	Cond. units.	Per cent.
4	172.8	62.2	216.8	61.0	263.5	60.0	2.93	1.69	3.11	1.43
8	190.7	68.7	239.7	67.5	291.4	66.4	3.27	1.71	3.45	1.44
52	218.5	78.7	276.9	77.9	340.2	77.5	3.89	1.78	4.22	1.52
128	244.0	87.9	310.1	87.3	384.0	87.5	4.41	1.81	4.93	1.59
512	262.9	94.7	334.7	94.2	414.6	94.4	4.79	1.82	5.33	1.59
2048	277.7	100.0	355.3	100.0	439.0	100.0	5.17	1.86	5.58	1.57

SUMMARY.

Glycerol solutions of the cobalt salts investigated were found not to show any of the fine red cobalt bands. Rise in temperature of the more concentrated solutions caused the yellow absorption band at λ 5100 to widen and to broaden out, so as finally to absorb all the red and thus cause the solution to appear blue.

Concentrated aqueous solutions of cobalt chloride show an enormous increase in the absorption with rise in temperature. Between quite narrow ranges of temperature there is a very great increase in the red absorption in the region of the finer bands. As the concentration is increased the temperature at which this great increase in the absorption takes place is lowered. For the more dilute solutions the widening of the absorption with rise in temperature is quite symmetrical.

The effect of rise in temperature on the absorption of cobalt nitrate and cobalt sulphate is quite small as compared with the effect on the chloride.

The presence of calcium or aluminium chloride with cobalt chloride in water causes the effect of temperature on the absorption to be greater, and causes the red absorption to take place in more dilute solutions, than it does in pure cobalt chloride solutions. The temperature at which the absorption in the red increases so greatly may be called the "critical color temperature."

The "critical color temperature" seems to depend upon the existence of some *solvate* or *peculiar condition of the cobalt molecule.* The critical color temperature is much higher in water and glycerol than for other solvents. In a similar manner the water and glycerol bands are more persistent than the alcohol or acetone bands. It is important that a complete study be made of the critical color temperature for the various cobalt salts, and for the same salt in different solvents and when mixed with other salts. At the same time a study of the characteristic cobalt bands could be made.

A preliminary test was made to find if the presence of NO_3 and water had the same hypsochromous effect[1] on the cobalt bands as it has on the uranyl bands. Unfortunately no bands of any strength have as yet been detected for cobalt nitrate in water.

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[1] Strong: Phys. Rev., 29, 555 (1909).

CHAPTER V.

NICKEL SALTS.

Introduction.—Nickel chloride.—Nickel sulphate.—Nickel acetate.—Conductivity data.

INTRODUCTION.

Among the more recent investigations on nickel salts may be mentioned those of Müller [1] and Jones and Anderson [2]. Müller found that Beer's law holds for solutions of nickel nitrate and sulphate, but that the chloride and bromide showed variations from the law. He concludes that both hydration and aggregation play a part in producing these variations from Beer's law.

Jones and Anderson [2] find that Beer's law holds for the chloride, sulphate and approximately for the acetate. Rather narrow bands were found at λλ 6110, 6250, and 6440 for a mixture of nickel and aluminium chlorides. This is another example of the effect of the presence of aluminium or calcium chloride. Further work should be done on the effect of the presence of these salts and of free hydrochloric acid. The investigations should be carried out at low temperatures.

NICKEL CHLORIDE.

A spectrogram showing the effect of rise in temperature was made for an aqueous solution of nickel chloride, 2.66 normal concentration and 3 mm. length of layer. The length of exposure to the Nernst glower was 2 minutes, current 0.8 ampere and slit-width 0.20 mm. The exposure to the spark was for 5 minutes. Starting with the strip next the numbered scale, the temperatures are —2°, 14°, 29°, 44°, 58°, 70°, and 84° C.

The absorption of nickel chloride consists of a band which absorbs the ultra-violet, violet, and blue portions of the spectrum. At the low temperatures there is a small transmission in the blue, but at −2° practically all light is absorbed up to λ 4200. As the temperature is raised the absorption extends towards the region of greater wave-lengths; at 44° it is at λ 4400 and at 84° at λ 4600. The transmission extends into the red as far as the films are sensitive.

A spectrogram (Plate 21, *B*) was made of an aqueous solution of a 2.66 normal concentration of nickel chloride of 2 mm. depth of layer. The length of exposure to the Nernst glower was 2 minutes and to the spark 6 minutes. The current through the Nernst glower was 0.8 ampere and the slit-width 0.20 mm. Starting with the strip adjacent to the numbered scale, the temperatures of exposure were 5°, 18°, 30°, 44°, 57°, 75°, and 85°.

At the lower temperatures there is complete absorption of almost all the shorter wave-lengths up to λ 4250 at 5°. There is an exception not shown in the printed spectrogram, and this is a very faint transmission

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[1] Ann. Phys., **12**, 767 (1903); **21**, 515 (1906).

[2] The Absorption Spectra of Solutions, Carnegie Institution of Washington Pub. No. **110**.

about λ 2800. With rise in temperature this transmission band gradually weakens and at 60° has practically disappeared.

The long wave-length edge of the absorption band widens uniformly with rise in temperature from λ 4250 at 5° to λ 4500 at 85°.

A spectrogram (Plate 21, *A*) was made of a 0.332 normal aqueous solution of nickel chloride of 16 mm. depth of layer. The length of exposure was 2 minutes to the Nernst glower, and 6 minutes to the spark. The current through the Nernst glower was 0.8 ampere and the slit-width 0.20 mm. Starting with the strip nearest the comparison spectrum, the temperatures of exposure were 5°, 19°, 33°, 45°, 60°, 71°, and 82°.

The absorption spectrum of nickel chloride under the above conditions consists of a band in the violet, and more or less complete absorption in the extreme ultra-violet. At 5° there is practically complete absorption to λ 2600. A diffuse absorption band runs from about λ 3700 to λ 4000. As the temperature is raised the transmission in the ultra-violet is somewhat increased. This is very peculiar, and is the first case thus far noticed of transmission increasing in the ultra-violet with rise in temperature. At 71° the violet band has widened out so as to extend from λ 3700 to λ 4250.

NICKEL SULPHATE.

A spectrogram (Plate 16, *B*) was made of the absorption spectra of a 2-normal aqueous solution of nickel sulphate 3 mm. deep. The length of exposure to the Nernst glower was 2 minutes and to the spark 6 minutes. The current through the glower was 0.8 ampere and the slit-width 0.20 mm. Starting with the strip nearest the comparison spectrum the temperatures were 5°, 19°, 32°, 47°, 61°, 72°, and 81°.

Nickel sulphate is remarkable for the fact that it has practically no absorption in the ultra-violet. The violet band at 5° extends from λ 3700 to λ 4200, and at 81° from λ 3700 to λ 4350. It will thus be seen that the effect of temperature on the absorption spectrum of nickel sulphate is very small and consists simply in the violet band widening slightly in the direction of the red.

NICKEL ACETATE.

A spectrogram (Plate 22, *A*) was made of a 0.5 normal aqueous solution of nickel acetate, the depth of layer being 9 mm. The length of exposure to the Nernst glower was 2 minutes, and to the spark 6 minutes. The current in the glower was 0.8 ampere and the slit-width 0.20 mm. Starting with the strip nearest the comparison spectrum, the temperatures were 6°, 23°, 38°, 52°, 64°, 74°, and 84°.

The absorption spectrum of nickel acetate is characterized by a band in the violet and a slight absorption in the ultra-violet. At 6° the absorption in the ultra-violet is very small. At 84° it extends to about λ 2600. At 6° the violet band runs from λ 3800 to λ 4150. There is considerable transmission in this region at the lower temperatures. At the higher temperatures the limits of this band are λλ 3700 and 4400.

A spectrogram (Plate 22, *B*) of a 0.5 normal solution of nickel acetate in water was made for various temperatures between 5° and 81°, the depth of layer being 3 mm.

At 5° there is almost complete transmission from λ 2300 to λ 7100. The only effect of rise in temperature was to increase slightly the absorption at the ultra-violet end of the spectrum and to weaken slightly the transmission in the region λ 4000.

NICKEL CHLORIDE IN WATER; CONDUCTIVITY AND DISSOCIATION.

Salts of nickel like those of cobalt are somewhat hydrolyzed at the higher temperatures and the higher dilutions.

V.	35°.		50°.		65°.		Temperature coefficients.			
							35° to 50°.		50° to 65°.	
	μv	α	μv	α	μv	α	Cond. units.	Per cent.	Cond. units.	Per cent.
4	174.9	61.1	218.0	59.3	266.0	58.4	2.87	1.64	3.20	1.46
8	194.5	67.9	247.3	67.2	301.5	66.2	3.52	1.81	3.61	1.46
32	225.5	78.8	288.1	78.3	354.7	77.9	4.17	1.85	4.44	1.54
128	251.4	87.8	321.4	87.4	398.4	87.5	4.66	1.85	5.13	1.59
512	270.6	94.5	344.4	93.6	426.1	93.5	4.92	1.82	5.45	1.58
2048	286.2	100.0	367.9	100.0	455.5	100.0	5.45	1.90	5.84	1.59

NICKEL NITRATE IN WATER; CONDUCTIVITY AND DISSOCIATION.

V.	35°.		50°.		65°.		Temperature coefficients.			
							35° to 50°.		50° to 65°.	
	μv	α	μv	α	μv	α	Cond. units.	Per cent.	Cond. units.	Per cent.
4	200.8	61.0	252.4	60.1	306.6	59.4	3.44	1.71	3.61	1.43
8	216.8	65.8	276.3	65.6	343.5	66.6	3.97	1.83	4.48	1.62
32	260.1	79.0	330.3	78.6	402.4	78.0	4.68	1.80	4.81	1.46
128	289.7	89.8	369.2	87.9	453.2	87.8	5.30	1.83	5.60	1.52
512	314.2	95.4	399.7	95.2	494.8	95.9	5.70	1.81	6.34	1.59
2048	329.3	100.0	(420.0)?	100.0	516.0	100.0	6.05	1.84	6.40	1.52

CHAPTER VI.

COPPER SALTS.

Copper bromide.—Copper nitrate.

A fairly concentrated solution of copper chloride or bromide is greenish brown, while dilute solutions are blue. The addition of aluminium or calcium chloride to a blue dilute solution of copper chloride changes the color to green. Uhler has investigated the effect of "dehydrating" agents, and also dissolved the copper salts in different solvents. Jones and Anderson have extended the investigations of Uhler. They consider that the ultraviolet band must be due to the copper molecule rather than to the ion. They consider from the way this band is affected by concentration that the absorbing power of the molecule is greatly affected by its immediate surroundings. The absorption band in the red, like the green cobalt band, they consider to be due to the metallic atom.

Copper Bromide.

Two spectrograms were made of the absorption spectra of copper bromide in water as affected by change in temperature. The first spectrogram (Plate 23, *A*) gives the absorption of a 2.06 normal solution of copper bromide 1 mm. thick and the second (Plate 23, *B*) a 0.25 normal solution 8 mm. thick. The time of exposure to the Nernst glower was 2 minutes, current 0.8 ampere and slit-width 0.20 mm. The time of exposure to the spark was 6 minutes. Starting with the strip nearest the comparison scale, the temperatures were 6°, 17°, 30°, and 45° for the concentrated solution, and 6°, 17°, 31°, 46°, 59°, 71°, and 85° for the dilute solution.

The effect of change in temperature on the absorption of light by this salt is very great, especially for the concentrated solutions. Above 45° not enough light was transmitted to affect the photographic plate in any part of the spectrum. At 6° a very faint transmission region runs from λ 5600 to λ 6600 for the 2.06 normal solution. At 45° there is a very feeble transmission about 200 Ångström units wide at λ 6400.

The dilute solution shows apparently complete transmission at 6° between $\lambda\lambda$ 3600 to 6800. As the temperature is raised this transmission band widens, and at 85° it extends from λ 4100 to λ 6700.

Copper Nitrate.

Two spectrograms were made of aqueous solutions of copper nitrate, the one (Plate 24, *A*) being 4.04 normal and having a depth of cell of 2 mm.; and the second one (Plate 24, *B*) being 0.505 normal and a depth of layer of 16 mm.; the amount of copper nitrate being the same in both cases. For the first spectrogram the time of exposure to the Nernst filament was 2 minutes and for the second spectrogram 3 minutes, the current being 0.8 ampere and the slit-width 0.20 mm. Starting with the strip adjacent to the comparison spectrum, the temperatures were 5°, 15°, 30°, 45°, 60°, 76°, and 87° for the concentrated solution, and 1°, 15°, 30°, 45°, 60°, 75°, and 82° for the dilute solution. At 5° the concentrated solution shows transmission from λ 3600 to λ 6500, at 87° from λ 3800 to λ 6000. For the dilute solution there is practically no change of absorption due to heating the solution from 1° to 82°. The transmission extends from λ 3550 to λ 6400.

A spectrogram (Plate 25, *B*) was made of a copper nitrate solution in water, 4.04 normal concentration and 3 mm. length of layer under the same conditions as for the other copper nitrate solutions. At zero temperature there was complete transmission from λ 3550 to λ 6000. At 82° the transmission extended from λ 3800 to λ 5900. The transmission spectrum was cut off quite sharply and completely in the violet, and the edge of transmission receded towards the red as the temperature was raised. The long wave-length edge of the transmission band was but slightly affected by change in temperature.

Hartley in his work on the effect of temperature on absorption spectra reaches the conclusion that the salt solutions that show the greatest change in their absorption spectra as the temperature is changed, are those that crystallize with the greatest amounts of water of crystallization. The copper salts show, however, that this is not the case; since of all these salts the bromide shows a very great coefficient of temperature change, while the nitrate shows a much smaller change. The copper salts are usually given the following formulas at ordinary room temperatures: $CuCl_2.2H_2O$; $CuBr_2.2H_2O$; $CuSO_4.5H_2O$; $Cu(NO_3)_2.3H_2O$. In many cases, however, Hartley's rule seems to hold quite well, and there is certainly no doubt that the water of combination plays a very important rôle in the absorption of light.

CHAPTER VII.

CHROMIUM SALTS.

Introduction.—Chromium chloride.—Chromium nitrate.—Chromium sulphate. Chromium acetate.—Chrome alum.—Conductivity data.

INTRODUCTION.

A fairly large number of investigators have worked on the absorption spectra of compounds of chromium. Some of these have studied the effect on absorption spectra of temperature, concentration, nature of the solvent, etc. In the following introduction to this chapter, a brief discussion of the work of Hartley, of Jones and Anderson, and of Bois and Elias is given.

Hartley found for the green chromium chloride that at 20° the bands were at λ 7040 to λ 6850, and λ 6730 to λ 5380. For chromium sulphate he found an absorption at λ 6000 at 100°, and at λ 5880 at 20°.

Violet chromium sulphate at 16° gave a band at λ 5430 (λ 5620 to λ 5250), and at 100° the band was at λ 5510 (λ 5770 to λ 5260).

Chromium nitrate, a violet-colored salt, at 16° gave an absorption band at λ 5920 (λ 6270 to λ 5570), and at 50° the position of the band did not change. Practically all of the light was absorbed at 100°.

A more dilute solution of chromium nitrate at 20° gave a band extending from λ 5880 to λ 5570. The position of this band did not change at 100°.

Chromium oxalate was found to give a band extending from λ 7060 to λ 6850 at 20°, and blue potassium chromoxalate $(K_6Cr_2)(C_2O_4)_6.6H_2O$, a band extending from λ 6270 to λ 4970 at 20°, and from λ 6310 to λ 5030 at 100°.

Red potassium chromoxalate $K_2Cr_2(C_2O_4)_4.10H_2O$ gave narrow bands at λ 6940 and λ 6850, and a band extending from λ 6330 to λ 4780 at 20°, and λ 5880 to λ 3570 at 100°.

Jones and Anderson[1] have photographed the absorption spectra of chromium chloride and nitrate in water. For chromium chloride they find large hazy bands at λ 4200 and λ 5900, and a much finer band at λ 6690. Chromium nitrate gives very similar bands at λ 4100, λ 5700, and λ 6690. It will be noticed that the wide nitrate bands have shorter wave-lengths than the corresponding chloride bands. The wave-lengths given by them for the wide cobalt bands bring out the same result. The cobalt chloride bands fall at λ 3300 and λ 5200, whereas for the nitrate the latter band lies at about λ 5100. The fact seems to be that the presence of the NO_3 group in some way causes the absorption bands to be shoved towards the violet. This is in accord with a paper by one of the authors,[2] where it was shown that the uranyl nitrate bands have shorter wave-lengths than the other uranyl bands. The same law was shown to hold for uranous bands and also for the phosphorescent bands of uranyl salts. The presence of free

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[1] Absorption Spectra of Solutions, Carnegie Institution of Washington Pub. No. 110.

[2] Phys. Rev., 29, 6, 555, Dec. (1909).

nitric acid causes the uranyl nitrate bands to shift still further towards the violet.

Bois and Elias[1] have investigated the effect of low temperature and a magnetic field on several chromium salts, and have made an especially detailed study of the ruby.

Chrome alum crystals ($KCr(SO_4)_2.12H_2O$) at 18° give a strong band from λ 6698 to λ 6716. At −190° this band has become smaller, λ 6684 to λ 6694, and is shifted about 17 Ångström units to the violet. A strong line appears at λ 6702 and about twenty bands occur between λ 6190 and λ 7160. The band λ 6686 to λ 6694 was slightly affected by a magnetic field. An aqueous solution shows bands at λλ 6627, 6723 and 6875, 7275.

Potassium chromium oxalate ($K_6Cr_2(C_2O_4)_6.6H_2O$) at 18° gives a band from λ 6980 to λ 7032; at −180° λ 6965 to λ 7012, a shift of 16 Ångström units. An aqueous solution gives bands at λλ 6953 to 6990 and 7084 to 7110. At 18° a glycerol solution gives a band at λλ 6946 to 6990. At −130° bands appear at λλ 6947, 6976; 6597, 6654; 6694, 6716; 6752, 6772.

The band λ 6925 of potassium chromium oxalate ($K_2Cr_2(C_2O_4)_4.xH_2O$) is slightly broadened by a magnetic field. Chromium fluoride mixed with borax gave at 18° two bands λλ 6734, 6810, and 6947, 7390; at −190° λλ 6724, 6805 and 6923, 7476; the first band thus shifting about 8 Ångström units to the violet.

The most important chromium compound investigated by Bois and Elias was the ruby, a solid solution of a small amount of Cr_2O_3 in aluminium oxide, Al_2O_3. Miethe[2] has found the absorption and fluorescent bands to occupy the same positions. The following data are taken from the paper of Bois and Elias.

Ordinary absorption spectra of the ruby.

At 18°.	At −190°.	Shift.
λ 4470 weak	λ 4465 weak	5.0
λ 4677 to λ 4691 weak band	λ 4675 to λ 4684 strong band	4.5
B_2 λ 4749 to λ 4757 strong band	λ 4746 strong line	7.0
B_1 λ 4765 to λ 4771 weak band	λ 4763 weak line	5.0
λ 5140 to λ 5995	λ 5028 to λ 5844	
	λ 5881 to λ 5912 strong band.	
	λ 5960 to λ 5974 strong band.	
λ 6575 to λ 6600 weak band	λ 6575 weak line	
	λ 6586 weak line	
λ 6666 to λ 6701 weak band	λ 6667 to λ 6689	
R_2 λ 6924 to λ 6926 strong band	λ 6918 strong line	7.0
R_1 λ 6938 to λ 6941 very strong band	λ 6932 very strong line	7.5

The extraordinary absorption spectra give considerable relative differences in the relative intensities of the absorption bands, but very little if any difference in the wave-lengths of the finer bands. The fluorescent bands excited either by arc or sunlight occupied the same positions as the absorption bands. A detailed account is given of the effect of magnetic fields of different strengths upon B_2, B_1, R_2, and R_1. The effect of a mag-

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[1] Ann. Phys., **27**, 12, 247 (1908).

[2] Verh. d. deutsch. physik. Gesell., **9**, 715 (1907).

netic field on R_1 as a fluorescent band was the same as on the absorption band, with the exception of the polarization. The effect of the magnetic field also seems to vary slightly with the temperature.

Chromium Chloride.

An aqueous solution of chromium chloride of 0.53 normal concentration and 2 mm. depth of cell shows the characteristic chromium bands. The solution in question had its absorption spectrum mapped between 5° and 83°. The ultra-violet band extended to about λ 2600, its edge being very broad. It was but slightly affected by the above change in temperature. The blue-violet band was broadened on its red side about 200 Ångström units by the above rise in temperature. The yellow band at 5° extended from λ 5500 to λ 6100. At 83° it extended from λ 5450 to λ 6200. There was but slight widening of this band with rise in temperature on the short wave-length side. The bands in the red do not appear.

A spectrogram was made of a 0.125 normal aqueous solution of chromium chloride 4 mm. depth of layer. Exposures to the Nernst glower were 3 minutes in length and to the spark 6 minutes. The current through the glower was 0.7 ampere and the slit-width 0.20 mm. The temperatures ranged between 4°, 20°, 35°, 50°, 61°, 73°, and 82°. At 4° the blue-violet band extended from λ 4200 to λ 4400, and the yellow band from λ 5200 to λ 6200. At 82° these bands had widened so that they extended from λ 4150 to λ 4550 and λ 5150 to λ 6400, respectively. At the highest temperature a weak band appears at approximately λ 6750. The band is very weak and diffuse.

A spectrogram was made of the change due to a rise in temperature on a 0.125 normal chromium chloride solution in water having a depth of layer of 4 mm. The solution of chromium chloride at room temperatures is a dull green. The length of exposure to the Nernst glower was 3 minutes, current 0.7 ampere and slit-width 0.20 mm. The length of exposure to the spark was 6 minutes. The temperatures, starting with the lowest strip, were 5°, 20°, 35°, 50°, 60°, 70°, and 82°.

At 5° the ultra-violet absorption was complete to λ 2600. At 82° this absorption had increased so as to extend to λ 2700. Over the remainder of the spectrum there was transmission. At higher temperatures the transmission was much weakened, however, at λ 4300, and in the whole region from λ 5000 to λ 6000.

Another spectrogram was made in exactly the same manner but with a deeper length of layer. At 5° the ultra-violet band for this solution reached to λ 2700, at 80° to λ 2800. There was more or less general absorption over the whole region of the spectrum, and this general absorption increased quite rapidly with rise in temperature, especially in the visible region. At the higher temperatures there was almost complete absorption at λ 4300 and from λ 5700 to λ 6100. These very diffuse bands broadened on both sides with rise in temperature, the broadening of the yellow-green band being, however, somewhat greater on the long wave-length edge. The characteristic bands in the red do not appear even at the higher temperatures.

Chromium Chloride and Aluminium Chloride.

A spectrogram (Plate 27, *A*) was made to show the effect of rise in temperature on a mixture of chromium chloride and aluminium chloride in water. The concentration of the former was 0.125 normal, and the latter 2.28 normal. The depth of cell was 9 mm. Exposures of 4 minutes were made to the Nernst glower and 6 minutes to the spark. The current through the glower was 0.8 ampere and the slit-width 0.20 mm. Starting with the strip nearest the comparison scale the temperatures were 6°, 19°, 36°, 51°, 66°, and 81°.

The most marked effect of the aluminium chloride was the production of a very pronounced unsymmetrical broadening. At 6° the ultra-violet band reached to λ 3000. At 81° it had widened to almost λ 3300, a greater widening than the same band in a pure chromium chloride aqueous solution. At 6° the blue-violet band extends from λ 4100 to λ 4600, and the yellow band from λ 5800 to λ 6200. The red sides of the blue-violet and yellow bands not only widen out enormously towards the red, but the short wave-length edges of these bands move towards the red. This effect is a continuous one, but is much greater for the temperature changes from 51° to 66° and 66° to 81°. At 81° the blue-violet band extends from λ 4150 to λ 5050, and the yellow band from λ 5900 throughout the remainder of the spectrum as far as the film is sensitive. The fine bands in the red do not appear.

Chromium Chloride and Calcium Chloride.

A spectrogram (Plate 27, *B*) was made of a mixture of chromium chloride and calcium chloride in aqueous solution, the chromium chloride being of 0.125 normal concentration and the calcium chloride of 3.45 normal concentration. The length of the solution was 9 mm. The exposures to the Nernst glower were for 5 minutes and to the spark 6 minutes. The current through the glower was 0.8 ampere and the slit-width 0.20 mm. Starting with the strip nearest the comparison scale the temperatures were 6°, 19°, 31°, 45°, 64°, and 80.

The effect of rise in temperature on this solution of chromium and calcium chlorides is very similar to that on chromium and aluminium chlorides. In this case the widening of the ultra-violet band is greater and practically all of this widening takes place in the change of temperature from 45° to 64° and from 64° to 80°. In this case the blue-violet and yellow bands widen unsymmetrically, and here too the short wave-length edge of the yellow band not only does not widen but actually narrows with rise in temperature. The blue-violet band widens on both edges, the greater widening, however, being on the red side.

At 6° the ultra-violet band extends to λ 2800, the blue-violet band from λ 4000 to λ 4400 and the yellow band from λ 5600 to λ 6100. At 64° the ultra-violet band extends to λ 3100, the blue-violet band from λ 4000 to λ 4600, and the yellow band from λ 5650 to λ 6300. At 80° the ultra-violet band extends to λ 3250, the blue-violet band from λ 3950 to λ 5000 and the yellow band from λ 5700 throughout the red end of the spectrum as far as the film is sensitive.

CHROMIUM NITRATE.

Two spectrograms were made of chromium nitrate in water, one (Plate 26, *A*) of a 0.754 normal concentration and 3 mm. depth of cell, and the other (Plate 26, *B*) a 0.094 normal concentration and 24 mm. depth of cell. The concentrated solution was exposed 2 minutes and the dilute solution 3 minutes to the Nernst glower, current 0.8 ampere and slit-width 0.20 mm. Both spectrograms were made using a 6 minutes exposure to the spark. Starting with the strip nearest the comparison scale the temperatures of exposure of the concentrated solution to the light were 5°, 17°, 32°, 45°, 60°, 70°, and 81°, and of the dilute solution 7°, 17°, 33°, 44°, 59°, 69°, and 83°.

Chromium nitrate under the conditions here described shows three bands, the NO_3 band in the ultra-violet, a band in the blue and violet and a wide band in the yellow and green. For the concentrated solution the temperature effect on the NO_3 band is small, the absorption being about 50 Ångström units greater at the higher temperature. At 5° the limit of this band is λ 3220. The blue-violet band extends from λ 3700 to λ 4500 and the yellow-green band from λ 5100 to λ 6300 at 6°. At 81° the blue-violet band extends from λ 3700 to λ 4600 and the yellow-green band from λ 5100 to λ 6450. For all the temperatures there was a band at about λ 6750. This band was unaffected by temperature.

At 7° the ultra-violet band of the more dilute solution extends to λ 3200 and is about 50 Ångström units wider at the higher temperature. The blue-violet band at 7° runs from λ 3650 to λ 4400, at 83° λ 3750 to λ 4600. The yellow-green band at 7° runs from λ 5400 to λ 6150. At 83° it has widened out from λ 5350 to λ 6400.

A spectrogram was made showing the effect of temperature on the absorption spectra of a 0.754 normal aqueous solution of chromium nitrate, the depth of layer being 1 mm. The times of exposure were 5 minutes to the spark and 2 minutes to the Nernst glower, current being 0.8 ampere and width of slit 0.20 mm. The temperatures, starting with the strip adjacent to the comparison spectrum, were 5°, 17°, 30°, 44°, 58°, 72°, and 82°.

The absorption spectrum of chromium nitrate under the above named conditions consists of a weak transmission band at λ 2800. At 5° this band is about 300 Ångström units wide. As the temperature is raised the transmission weakens, but there is so much general transmission that the stronger spark lines usually show more or less evenly throughout the absorption, which at 5° extends from λ 3000 to λ 4200. At 82° there is a complete absorption of all the short wave-lengths up to λ 4500. Like all other bands for chromium solutions, the edges are very broad and diffuse. At the higher temperatures there seemed to be somewhat greater absorption in the red at λ 6800.

CHROMIUM SULPHATE.

A spectrogram (Plate 28, *B*) was made of an aqueous solution of chromium sulphate of 0.125 normal concentration and a depth of cell of 3 mm. The length of exposure was 4 minutes to the Nernst glower at 0.8 ampere, and 6 minutes to the spark. The slit-width was 0.20 mm. The temperatures, starting with the strip nearest the numbered scale, were 5°, 20°, 37°, 51°, 66°, and 82°.

At 5° the three characteristic chromium bands appear—the ultra-violet band extending to λ 2800, the blue-violet band from λ 4100 to λ 4450 and the yellow-green band from λ 5500 to λ 6200. The bands at λ 6800 appear but very faintly. Throughout the visible portion of the spectrum there is a very strong absorption, as will be noticed from the extremely long exposure of 4 minutes to the Nernst glower.

At 82° the ultra-violet band extends to λ 2900, the blue-violet band from λ 4100 to λ 4550 and the yellow-green band from λ 5500 to λ 6300. The effect of temperature was very small, being in general the shifting of the long wave-length edges of all three bands towards the red.

CHROMIUM ACETATE.

A spectrogram showing the effect of rise in temperature on the absorption spectra of a 10 mm. solution of 0.125 normal chromium acetate was made. The slit-width was 0.20 mm. Exposures were made to the Nernst glower for 4 minutes, the current being 0.8 ampere. Exposures to the spark were continued for 6 minutes. Starting with the strip nearest the comparison scale, the temperatures were 5°, 20°, 36°, 52°, 64°, and 78°. The absorption remained practically independent of the temperature.

Chromium acetate under the present conditions of concentration and depth of cell shows a faint transmission band in the green between λλ 5000 and 5200. Except for a few faint bands there is transmission of all the longer wave-lengths beyond λ 6400. The whole blue, violet, and ultra-violet regions are absorbed, as is also the whole region between λ 5200 and λ 6400. There is an absorption band at λ 6490, which resembles very much one of the larger uranyl bands. It is about 60 Ångström units wide. The short wave-length edge of this band is very diffuse and looks very much as though the band were complex. There is a narrow band at λ 6550. This band is but 10 Ångström units wide. Narrow bands very much like this one appear at λλ 6510, 6800, 6860, 6920, 6970, and 7030. The smaller bands are very faint and in the spectrum-strip at 78° practically disappear.

A spectrogram was made of chromium acetate, 0.125 normal concentration in water and 3 mm. depth of cell. The exposures were 3 minutes to the Nernst glower at 0.8 ampere, and slit-width 0.20 mm. The length of exposure to the spark was 6 minutes. The temperatures were 5°, 19°, 37°, 50°, 64°, and 79°.

The effect of change in temperature in this chromium salt was very small, the only noticeable change being a slight increase in the intensity of the yellow band. The whole ultra-violet was absorbed up to λ 3800. From λ 3800 to λ 4600 there was a very strong general absorption. There was also strong absorption in the yellow.

CHROME ALUM.

A spectrogram (Plate 28, *A*) gives the effect of rise in temperature on the absorption spectra of chrome alum. It will be seen that the violet and ultra-violet bands are widened but slightly. The other chromium band in the yellow is slightly widened.

CHROMIUM CHLORIDE IN WATER—CONDUCTIVITY AND TEMPERATURE COEFFICIENTS.

Chromium chloride is considerably hydrolyzed at the higher dilutions, and at the higher temperatures. The temperature coefficients are, therefore, not quite as regular as with the other salts, and even approximate dissociations can not be calculated.

V.	35°.	50°.	65°.	Temperature coefficients.			
				35° to 50°.		50° to 65°.	
	μv	μv	μv	Cond. units.	Per cent.	Cond. units.	Per cent.
4	201.3	259.8	329.9	3.90	1.94	4.67	1.80
8	240.1	313.4	395.9	4.88	2.03	5.50	1.75
32	301.1	391.0	489.0	5.99	1.99	6.53	1.67
128	369.5	483.3	615.6	7.59	2.05	8.82	1.82
512	438.6	590.1	761.6	10.10	2.30	11.43	1.94
2048	523.5	686.0	871.1	10.83	2.06	12.34	1.80

CHROMIUM NITRATE IN WATER—CONDUCTIVITY AND TEMPERATURE COEFFICIENTS.

Results of the same general character were obtained with chromium nitrate as with chromium chloride. On account of the hydrolysis it was impossible to calculate the dissociation.

V.	35°.	50°.	65°.	Temperature coefficients.			
				35° to 50°.		50° to 65°.	
	μv	μv	μv	Cond. units.	Per cent.	Cond. units.	Per cent.
4	228.2	289.7	365.2	4.10	1.80	5.03	1.73
8	263.0	334.7	419.4	4.78	1.82	5.65	1.69
32	321.4	414.8	519.1	6.23	1.94	6.95	1.68
128	395.0	517.6	663.2	8.17	2.07	9.71	1.87
512	473.2	627.6	809.0	10.23	2.18	12.09	1.93
2048	554.3	732.6	937.4	11.88	2.14	13.65	1.86

CHAPTER VIII.

ERBIUM SALTS.

Introduction.—Erbium chloride in glycerol.—Erbium chloride in water as affected by rise in temperature.—Erbium nitrate and other salts.

Of all compounds known those of erbium probably show the most characteristic absorption spectra in the solid state and in solution. The first to make a detailed study of the erbium spectrum was H. Becquerel.[1] One of the minerals that he studied was xenotine or hussakite, a uniaxial crystalline compound consisting mainly of the phosphates of yttrium and erbium. The wave-lengths of the ordinary and extraordinary spectrum bands are given. The absorption spectrum observed in any direction through the crystal Becquerel found to be made up by the superposition of two series of bands, one corresponding to vibrations normal to the axis of the crystal and the other to vibrations parallel to this axis.

Schulz[2] has worked on the effect of a magnetic field on the absorption spectrum (obtained by reflection) of erbium oxide. He finds that the bands $\lambda\lambda$ 4482.2, 4491.3, 4510.5, 4541.9, 4554.1, 4562.6, 4571.8, 4579.1, 4606.5, 4625.9, 5197.0, 5205.5, 5242.2, 5261.0, 5387.7, 6430.0, 6476, 6496, 6524, 6538, 6546, 6562, 6581, 6598, 6617, and 6652 broaden when the magnetic field is turned on; λ 4482.2 is shifted to the red, while λ 4510.5 and λ 4562.6 are shifted towards the violet.

Bois and Elias[3] have made a very thorough study of the absorption of hussakite, erbium yttrium sulphate, erbium nitrate and erbium magnesium nitrate at 18° and at $-190°$ and also found the Zeeman effect at these temperatures. As the results are all collected in the above reference no detailed account will here be given. In general, the bands show a Zeeman effect. Doublets and triplets are quite common.

A very extended investigation on the effect of low temperatures and magnetic fields on the absorption spectra of erbium has been made by J. Becquerel. As the papers of Becquerel are somewhat scattered, a rather full account of them will be given here. The first work[4] of Becquerel was upon the effect of a magnetic field on the absorption spectra of xenotine and tysonite at ordinary temperatures. In the following table + will signify a strong band and + + a very strong band. Field will always refer to the magnetic field which in this work is usually 14,100 c.g.s. units. Units of wave-length are stated in Ångström units.

When the optic axis is parallel to the beam of light a crystal behaves like an isotropic body. When placed in a magnetic field, however, a rectilinear vibration is transformed into an elliptical one. This is Becquerel's magnetic double-refraction. The effect of the magnetic field on vibrations normal to the field is different from the effect on vibrations parallel to

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[1] Ann. Chim. Phys. (6), 14, 194 (1888).

[2] Astrophys. Journ., 30, 383 (1909).

[3] Ann. Phys., 27, 279 (1908).

[4] Compt. rend., Mar. 26, Apr. 21, May 21, Nov. 19, Dec. 3, Dec. 10, Dec. 24 (1906); Jan. 21 (1907). Le Radium, Feb. (1907).

XENOTINE.

Wave-lengths.		I. Optic axis parallel to field.		II. Optic axis parallel to light beam.		III. Optic axis normal to field and light beam.*
Ordinary spectra.	Extraordinary spectra.	(*a*) Ordinary vibrations normal to the field.	(*b*) Extraordinary vibrations.	(*c*) Ordinary vibrations normal to the field.	(*d*) Ordinary vibrations parallel to the field.	(*e*) Extraordinary vibrations normal to the field.
5206.5++		Doubles symmetrically		Doubles dis. sym., 3.1 A. U.	Spread out towards violet.	
	5206.7++		Broadens unsym			Doubles 3.7 unsym.
5211.3++		Broadens sym		Doubles	Broadens.	
5215.5++		Do.		Displaced to red	Doubles 3.7.	
	5220.1++		Broadens unsym			Broadens to red.
5221.5++		Doubles 5 9 sym	Displaced 1.0 to violet.	Displaced to violet		
5225.6		Doubles 5.1 sym		Displaced 1.0 to violet	Displaced to violet.	
5236.6++		Broadens sym		Broadens	Doubles symmetrically	
	5237.2++		Broadens			Broadens.
5242.0++		Broadens sym		Broadens	Broadens.	
5245.8+		Broadens		Doubles unsymmetrically	Do.	
5251.1	5251.1++	Doubles 2.6	Broadens	Do.		Doubles unsymmetrically
	5268.0+		Do.			
	5388++ 5394++		Doubles unsym			Spread out towards violet.
6422.7		Doubles 8.9		No change.		
	6424 6++		Broadens			
6434.5		Doubles 7.7		No change.		
	6435.8++		Doubles 9.6 unsym			
	6463		Doubles unsym			Broadens.
6505.6+	6504.5	Doubles symmetrically		Doubles 3.8 unsymmetrically	Spread out towards violet.	
6523.4++	6528.2	Do.		Doubles 4.4 unsymmetrically	Spread 3.0 towards violet.	
6537.0+	6538.0			Displaced 2.0 to red	Doubles 6.6 unsym	Displaced to violet.
	6542.8++		Doubles 4.7 sym			Do.
6542.5						
	6563		Displaced to violet			Broadens.
6564.4+		Doubles 4.4 sym		Doubles 4.6 unsym		
	6573.++		Doubles 4.3 sym			Spread out towards red.
6571.6		Displaced 1.7 to red			Displaced to violet.	
6581.0+		Broadens sym		Weakened	Spread out to violet.	

* Ordinary vibrations parallel to the field are the same as those under II *d*.

the field. A crystal less than 1 mm. thick in a field of 2720 c.g.s. units causes a difference of $\frac{1}{3}\lambda$ in the middle of some bands.

To explain the Zeeman effects observed we must consider whether the external field is simply added to the intramolecular fields, or whether there are variations produced there by the presence of the atoms. If one assumes the same vibrators in every case, electrons with a value of e/m of 1.8 $(10)^7$, then the internal magnetic fields must vary between 200,000 c.g.s. units in one direction and about the same number of units in the opposite direction. Assuming, on the other hand, that the intra-atomic field simply has the external magnetic field added then Becquerel gives the following values of $e/m = 2\pi V \frac{d\lambda}{\lambda^2} \frac{1}{H}$, + referring to a positive electron:

λ 5206.5^{++}, $e/m = +4.5\ (10)^7$;
λ 5211.3^{++}, $-0.3\ (10)^7$;
λ 5215.5^{++}, $+2.1\ (10)^7$;
λ 5221.5^{++}, $+1.6\ (10)^8$;
λ 5225.6, $-1.4\ (10)^8$;
λ 5236.6^{++}, $+2.9\ (10)^7$;
λ 5242.0^{++}, $+1.9\ (10)^7$;
λ 5245.8^{++}, $+4.5\ (10)^7$;
λ 5251.1, $-7.1\ (10)^7$;
λ 6422.7, $-1.6\ (10)^8$;
λ 6434.5, $-1.4\ (10)^8$;
λ 6474.0, $+3.8\ (10)^7$;
λ 6505.6^{+}, $+5.1\ (10)^7$;
λ 6523.4^{++}, $-5.9\ (10)^7$;
λ 6537.0^{+}, $-2.8\ (10)^7$;
λ 6542.5, $+3.4\ (10)^7$;
λ 6564.4^{+}, $-8.6\ (10)^7$;
λ 6581.0^{+}, $+3.6\ (10)^7$.

For convenience we will consider that some of the above bands are due to + electrons, and some due to − electrons, according to the value of e/m as calculated from the above formula.

The magnetic rotatory polarization is very closely related to the Zeeman effect, the + and − electrons behaving differently in this case also; the sense of the rotation being different for the + and for the − electrons.

J. Becquerel, in Le Radium, March, 1907, gives a theory for the magnetic optical effects which are observed in crystals. The general basis of his theory is somewhat similar to that of Voigt.[1] The electrons are considered to move along each coördinate axis independently. The three directions are considered to be the same for each electron and independent of the period of the exciting light. The form of the equations is then similar to those of a pendulum experiencing great frictional resistance. The theory as here developed explains some but not all of the different types of resolution found experimentally. As different results have been obtained, especially by Page,[2] the development given by Becquerel will not be considered in detail.

Later papers by Becquerel[3] deal with the effect of a magnetic field on the absorption spectra of certain crystals of xenotine, tysonite, parisite, monazite, apatite, and zircon at low temperatures. The bands in general are displaced towards the violet, especially for tysonite, as the temperature is lowered. Many changes of relative intensity occur and at low temperatures the bands are invariably narrower and more intense.

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[1] Ann. Phys., 6, 346 (1899); 6, 784 (1901); 8, 872 (1902).

[2] Trans. Camb. Phil. Soc., vol. **20**, No. **13**, 291, 322.

[3] Compt. rend., Feb. 25, Mar. 25, May 13, June 17, Aug. 19 (1907); Le Radium, Sept. (1907).

For xenotine the following table is given:

Ordinary spectra.		Extraordinary spectra.	
λ at 25°.	Displacement between 25° and −188°.	λ at 25°.	Displacement between 25° and −188°.
5206.5	Doubled, 0.4 to violet.....	5206.7	0.4 to violet.
5211.3	1.5 to violet.............	5220.1	1.5 to violet.
5215.5	0.5 to violet.............		
5221.6	0.1 to violet.............		
5236.6	0.5 to red................	5237.2	0.5 to red.
5242.0	0.9 to red................	5251.1	0.6 to red.
5245.8	0.5 to red................		
5251.1	0.6 to red................	5268	0.4 to violet.

There does not seem to be any relation between the Zeeman effect and the effect due to change in temperature. Becquerel also states that the Zeeman effect is independent of the temperature. Related bands are usually affected in the same way by change in temperature.

In the introduction the ordinary equation of an electron considered in the theory of dispersion was:

$$m\ddot{x} + \kappa\dot{x} + n^2x = eE \cos pt$$

The resistance $\kappa\dot{x}$ designates a mean resistance, and causes the decay of the light vibration. It may result from sudden shocks undergone in any irregular or fortuitous manner by any of the electrons taking part in the absorption of light. The greater κ is the wider the band will be. The above equation leads to a value of the refractive index μ.

$$\mu^2(1-\kappa^2) = 1 + \Sigma \frac{e_h\partial^2(\partial^2 - \partial_{0h}^2)}{(\partial^2 - \partial_{0h}^2) + \partial^2\,\partial_h^{12}}$$

κ is the coefficient of absorption; $2\,\pi\,\partial_{0h}$ is the period corresponding to the middle of an absorption band h; e_h is a coefficient depending on the substance and the band.

$$e_h = \frac{4\pi V^2 e^2/N_h\partial_{0h}^2}{m_h}$$

N_h is the number of electrons h/cc.; $\partial_h^1 = \frac{\kappa_h}{m_h}\partial_{0h}^2$. Becquerel has obtained the value of the ratio of ∂^1 at 20° and at −186°. The bands are those of tysonite.

λ at 20°.	Ratio of δ′.
4791 spec. extraord	1.83
5176 spec. ord..........	1.84
5235 spec. ord..........	1.83
5825 spec. ord..........	1.85

The ratios of ∂' are very nearly the same as the ratios of the square roots of the absolute temperature. The width of the bands measured between the maxima of the deviations of the dispersion curve vary directly as the square root of the absolute temperature.

If this law is true then the size of the bands is proportional to the mean speed of translation of the molecules. Schönrock[1] has shown that the width of bands in a gas results not only from the Döppler effect due to the kinetic motion of the gas molecules, but also from collisions. Collisions determine the sudden and fortuitous variations in the phase, amplitude, and direction of motion of the electrons, and prevent the light that is being emitted or absorbed from being homogeneous. The size of the bands is then a function of the mean length of the wave-trains emitted between collisions. If ∂ is the width of the band between the positions where the intensity of light is half the maximum, and r is the length of the train of waves emitted between collisions, then:

$$\partial = \frac{1.39\,\lambda_0^2}{\pi r} = \frac{1.39\,\lambda_0^2 u}{\pi v L} = A\,\frac{\lambda_0^2}{L}\sqrt{\frac{T}{M}}$$

u is the mean speed of translation, L the mean free path, v the velocity of light, A is a constant, M the molecular weight, T the absolute temperature; $L = l^2/\rho^2\sqrt{2\pi}$, l is the mean distance between the centers of molecules; ρ is the distance between two molecules at the time of their collision.

If the same mass and volume of a vapor has its temperature raised, l and ρ are but slightly changed, so that the width of the bands should vary as the square root of the absolute temperature. The above theory applies to a gas. The width of the bands of solids can not be explained on the Döppler-Fizean principle, but may be due to the extremely numerous shocks of the molecules. The fineness of the erbium bands may then be due to the union of several atoms into big molecules having a very small velocity of translation. If the molecules are large the collisions will be less numerous.

In a later paper Becquerel[2] gives some values for the terms which appear in his equation giving the refractive index. It should be stated here that dispersion equations differ considerably according to the assumptions made in their calculation.

TYSONITE.

λ at 25°.	*lh* at 25°.	*lh* at −188°
4791	2.29 $(10)^{-7}$	7.23 $(10)^{-7}$
5176	2.14 $(10)^{-7}$	5.31 $(10)^{-7}$
5235	.71 $(10)^{-7}$	1.53 $(19)^{-7}$
5825	4.82 $(10)^{-7}$	2.35 $(10)^{-7}$

From the changes of *lh*, the dielectric coefficient, with changes in temperature, Becquerel considers that the increase in intensity of the bands when the temperature is lowered is not only due to a narrowing of the bands, but also to an increase in the total amount of energy absorbed as the dielectric constant is increased. Let us assume that $e = 3.4\ (10)^{-10}$.

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[1] Ann. Phys., **20**, 995 (1906); **22**, 210 (1907).
[2] Le Radium, Nov. (1907).

TYSONITE

	λ 5176.	λ 5235.
e/m	$+2.49\ (10)^{7}$	$-2.48\ (10)^{7}$
Ne at 25° U. E. M.	$1.01\ (10)^{-5}$	$3.28\ (10)^{-6}$
Ne at −188°	$2.50\ (10)^{-5}$	$7.07\ (10)^{-6}$
Nm at 25°	$4.05\ (10)^{-13}$	$1.32\ (10)^{-13}$
Nm at −188°	$1.00\ (10)^{-12}$	$2.85\ (10)^{-13}$
N at 25°	$0.89\ (10)^{15}$	$2.9\ (10)^{14}$
N at −188°	$2.21\ (10)^{15}$	$6.25\ (10)^{14}$

From the above, then, N, the number of absorbing electrons increases as the temperature is lowered. The number of absorbing electrons is very much smaller than the number of atoms present. Hallo[1] and others have shown that only a small number of sodium atoms take part in the absorption of the two D lines.

D_2 (Hallo) . . . . $e_{0_2} = 7.5\ (10)^{-8}$ $N_{0_2} = 3.3\ (10)^{14}$
D_1 (Gerst) . . . . $e_{0_1} = 2.1\ (10)^{-7}$ $N_{0_1} = 1.1\ (10)^{15}$
λ 5221.5 (Xenotine) . . . . $e_{25°} = 5.43\ (10)^{-8}$ $N_{25°} = 3.34\ (10)^{13}$
$e_{-188°} = 9.68\ (10)^{-8}$ $N_{-188} = 5.96\ (10)^{13}$

The index of refraction of solids, and especially minerals, changes very little with change in temperature, so that the electrons influencing refraction are but slightly affected by changes in temperature. Drude, Cheveneau,[2] and others have shown that the number of these electrons vibrating in the ultra-violet is approximately that of the valencies of the atoms composing the molecule.

Becquerel[3] has continued his work at low temperatures, doing part of the work with Onnes[4] at Leyden. One of the problems arising from Becquerel's work is whether the paramagnetism of erbium and neodymium affects the internal magnetic fields which would exist within the crystals if they were diamagnetic. For this reason the Zeeman effect is found for widely different temperatures. If the Zeeman effect is independent of temperature then one would consider that paramagnetism did not play a very important rôle. Becquerel finds the Zeeman effect on the bands of xenotine and tysonite to be independent of the temperature.

In a table giving the Zeeman effect on tysonite and parisite it is seen that bands that are in practically the same portion of the spectrum are affected in a very different way by the magnetic field. From the Zeeman effect the following erbium alcohol bands are due respectively: λ 4870 to −; λ 4880 to −; λ 5238 to +; and λ 5410 to − electrons.

Considerable data are given by Becquerel upon the rotatory magnetic polarization. The results confirm the theory of the Hall effect—that the sense of the dispersion is just the opposite on the outside of the band from what it is on the inside. Applying the theory to the band λ 5221.5 of xenotine, Becquerel obtains the results shown in the following table:

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[1] Arch. Néerlandaises (2), t. 10, p. 148 (1905).
[2] Le Radium, June (1907).
[3] *Ibid.*, Jan. (1908); Nov. (1909); Compt. rend., Dec. 9, 30 (1907).
[4] *Ibid.*, Aug. (1908).

	H.	e/m.	N_e.	N_m.	N.
Temperature 20°.......	14,100	$1.656\ (10)^8$	$3.78\ (10)^{-7}$	$2.28\ (10)^{-15}$	$3.34\ (10)^{13}$
Temperature —188°....	12,300	$1.656\ (10)^8$	$6.74\ (10)^{-7}$	$4.07\ (10)^{-15}$	$5.96\ (10)^{13}$

Erbium Chloride in Glycerol.

Several photographs (Plate 29, *A* and *B*) were made of the absorption spectra of erbium chloride dissolved in glycerol. The absorption is very similar to that of an aqueous solution; the bands, however, in general being shifted towards the red. The bands shown by a solution 30 mm. in depth are located as follows: λ 3250; λ 3370; λ 3510. These three bands are quite strong, being some 30 or 40 Ångström units wide; λ 3600 is weak and narrow; λ 3650 is quite strong; λ 3785 is quite strong; λ 3885 is considerably weaker than the five other ultra-violet bands described above; λ 4165; λ 4490 and λ 4520 are of about equal intensity and quite strong (in the region near these bands there are numerous weak bands and these would come out better if a greater depth of cell could have been used, but on account of the slight solubility of erbium chloride in glycerol the use of a greater cell-depth was not practicable); λ 4910 weak; λ 5190; λ 5210; λ 5225 rather strong; λ 5240 weak; λ 5260 weak; λ 5380; λ 5420; λ 5440; λ 6450; and λ 6530. The measurements were from a spark-line at λ 3995 and hence are more accurate in this region. On the whole, most of the erbium chloride bands are of greater wave-length for the glycerol solution than for the aqueous solution.

The relative intensities of the water and glycerol bands differ considerably, but the wave-lengths do not appear to be very greatly changed. The photographic films appear to have contracted differently on drying, so that no very accurate comparisons of the wave-lengths of the water and glycerol bands could be made.

Rise in temperature from 15° to 200° produces no noticeable change in wave-length. At the higher temperature the bands are very much less distinct and apparently considerably weaker. For instance, the group of bands at 15° at λ 5200 practically becomes a single hazy band at 200°.

Erbium Chloride in Water, Effect of Temperature.

A spectrogram (Plate 30, *B*) was made to show the effect of rise in temperature on the absorption spectrum of an aqueous solution of erbium chloride. For this purpose a 0.94 normal solution was used and the depth of layer was 48 mm. The solution probably contained a considerable number of impurities, so that the amount of erbium was in fact quite small. The absorption spectrum was found to change but little with rise in temperature, thus indicating a dilute solution. Exposures were made for 30 seconds to the Nernst glower and 4 minutes to the spark. The current through the glower was 0.8 ampere and the slit-width 0.20 mm. Starting with the spectrum nearest the comparison scale, the temperatures were 7°, 17°, 29°, 46°, 60°, 70°, and 80°.

At 70° the ultra-violet is absorbed to λ 3950. As the temperature is raised the ultra-violet absorption increases, and at 80° it reaches λ 3150.

Bands from 20 to 40 Ångström units wide occur at λ 3235, λ 3510, λ 3640 and λ 3785. These bands are slightly wider at 80°, but as for all the other erbium bands this widening is very small. Weak and narrow bands appear at λλ 4165, 4425, 4458, 4500 (strong), 4535, 4540, 4555, 4580, 4685, 4750 (30 Ångström units wide), 4810, 4840, 4855, 4870 (strong and 20 Ångström units wide), and 4920. λ 4920 lies alongside of a fuzzy band extending from λ 4910 to λ 4950.

After these comes a rather wide band which for a shorter length of layer would most likely be broken up into a number of much finer bands. This band extends from λ 5190 to λ 5250. At λ 5217 a narrow, sharp line runs through the fuzzier and wider band. Broad (about 30 Ångström units wide) and very faint bands are located at λ 5630 and λ 5760. For greater concentrations these would probably show as finer bands. The band at λ 6540 is much more diffuse on the red than on the violet side; this possibly being due to a component that is not separated at this temperature. Other bands are located at λλ 5365, 5380, 5425, 5445, 5505, 6410, 6440, 6495, and 6690. The general effect of rise in temperature here is to cause the lines to become slightly fuzzier and to show more of a "washed-out" appearance. No shift or rise in temperature was noticed.

ABSORPTION SPECTRA OF ERBIUM NITRATE AND OTHER SALTS OF ERBIUM.

It was thought to be of interest to test whether the NO_3 group had any hypsochromous effect on the absorption spectra of aqueous solutions of erbium salts. The following approximate wave-lengths of the bands do not show any such hypsochromous effect as was found for the uranyl bands:

Erbium nitrate.	Erbium chloride.	Erbium nitrate.	Erbium chloride.	Erbium nitrate.	Erbium chloride.
3630	3635	4270‡		5210	5205
3760*		4425	4415	5235	5230
3788†	3785	4480§		5365	5365
3880‡		4500	4905	5420	5415
4045		4675§	4670§	6400	6410
4070		4730§		6480	6490
4160	4150	4850	4845	6530	6535
4190		4870	4865		
4215	4210	4910§	4905		

* Hazy. † Strong. ‡ Wide and weak. § Weak.

The crystals of erbium sulphate have a fine absorption spectra. As the water of crystallization is driven off the bands change very considerably and become much more diffuse. The reflection spectrum from fused erbium oxide consists of a large number of fine lines. As shown by Anderson, these lines become wider as the temperature is raised, until they become emission bands. The emission bands are quite broad. Between 100° and 600° some of the fine erbium bands shift about 10 Ångström units. The difference between the wave-lengths of the emission bands and the absorption bands at high temperatures is hidden by the haziness of the bands if it exists at all.

CHAPTER IX.

PRASEODYMIUM SALTS.

Introduction.—Praseodymium chloride.—Praseodymium nitrate.

INTRODUCTION.

Very little work has been done upon praseodymium compounds, for the reason that the absorption bands are much wider than those of erbium or neodymium. Bois and Elias have worked on $Pr_2(SO_4)_3 8H_2O$. At −190° they found bands at λλ 5990 to 5993 and λλ 6009 to 6014. These bands broadened slightly when a magnetic field of 40,000 c.g.s. units was applied. The widening was much less than that obtained by Becquerel for neodymium bands.

Jones and Anderson found that the ultra-violet band λ 3000 was a "methyl alcohol" band and was very weak for aqueous solutions, if it existed at all. They think that there are other "alcohol" bands, but that they are not far enough separated from the "water" bands to appear by themselves. Similar results are found in the region λ 5900.

PRASEODYMIUM CHLORIDE.

A spectrogram (Plate 31, *A*) was made of a 2.56 normal aqueous solution of praseodymium chloride 3 mm. deep. Exposures were made to the Nernst glower (current 0.8 ampere and slit-width 0.20 mm.) for 20 seconds. The time of exposure to the spark was 4 minutes. Starting with the strip nearest the numbered scale, the temperatures were 7°, 23°, 40°, 52°, 68°, and 84°.

The ultra-violet is absorbed up to λ 2700 and this absorption does not vary greatly with temperature, increasing slightly, however. At 7° there are bands from λ 4385 to λ 4500, λ 4640 to λ 4720, λ 4810 to λ 4845, λ 6860 to λ 6990. This latter band is double, the red component being much the narrower and having its center at λ 6980. Throughout the remainder of the spectrum there is complete transmission.

At 84° the absorption bands are located at λλ 4380 and 4510, λλ 4640 and 4730, λλ 4810 and 4845, and λλ 6870 and 6775. The bands all widen slightly except the latter. At 7° the latter band consisted of two separate bands. At 84° the λ 6980 band has diffused into the other band and the general transmission throughout the band has been greatly increased. In this respect this band is very peculiar indeed, and behaves with respect to temperature changes in just the opposite way from practically all other bands investigated.

A spectrogram (Plate 31, *B*) was made of a 0.043 normal aqueous solution of praseodymium chloride 196 mm. deep. This spectrogram was to show whether changes due to temperature in the spectrogram were affected by the concentration of the solution. The length of exposures to the Nernst glower (current 0.8 ampere and slit-width 0.20 mm.) was 20 seconds. The length of exposure to the spark was 4 minutes. Starting with the strip nearest the comparison spectrum, the temperatures were 7°, 20°, 36°, 51°, 66°, and 82°.

The absorption spectrum of the dilute solution is practically the same as that for the concentrated solution. At 7° bands occur from λ 4385 to λ 4490, λ 4640 to λ 4715, λ 4810 to λ 4840, λ 5860 to λ 5940 and a narrow band at λ 5980.

The ultra-violet absorption at 7° extends to λ 2650; at 82° it extends to λ 2750. The other bands are at λλ 4385, 4490, 4650, 4715, λλ 4805 to 4835, λλ 5870 to 5930. The band λ 5980 has become much more diffuse. The band adjacent to it has also become narrower and much more filled up by general transmission than at the lower temperatures. It will be seen in general that there is very little if any temperature change in the absorption bands of praseodymium chloride at this concentration, except the bands in the red, which become narrower and weaker at the higher temperatures. In the concentrated solution the change in this band was not as great as in the dilute solution. In the concentrated solutions the other bands widened slightly more than they do in the solution here described.

The spectrogram (Plate 32, *B*) of an aqueous solution of praseodymium chloride shows the effect of change in temperature between 7° and 84° on a 2.56 normal solution 48 mm. deep. The exposure to the Nernst glower (current 0.8 ampere and slit-width 0.20 mm.) was for 20 seconds. The exposure to the spark was for 4 minutes. Starting from the comparison spectrum, the strips were taken at the temperatures 7°, 20°, 35°, 51°, 66°, and 84°.

The spectrum-strip at 7° shows a large band in the blue and one in the yellow. There is absorption in the ultra-violet. In the case of praseodymium nitrate the absorption in the ultra-violet was probably due to the NO_3 band. This absorption was found to be unaffected by temperature. In the case of praseodymium chloride the absorption increases very markedly with rise in temperature. At 7° the limits of the blue band are $\lambda\lambda \left\{ \begin{matrix} 4280 \\ 4270 \end{matrix} \right\}$ and $\left\{ \begin{matrix} 4940 \\ 4930 \end{matrix} \right\}$ and for the yellow band λλ 5750 and 6100. There is slight absorption in the region λ 5000 to λ 5100, which is probably due to absorption bands. Two fine bands, each about 8 Ångström units wide, appear at λλ 5220 and 5235. Absorption of the shorter wave-lengths at 7° is complete to λ 3100, at 51° λ 3200, and at 84° λ 3300. At 51° the blue band is located at λλ 4280 and 4950, and the yellow band at λλ 5740 and 6110.

At 84° the limits of the blue band are λλ 4280 and 4950, and of the yellow band λλ 5750 and 6110. The widening of the bands is very small indeed. The fine bands λλ 5220 and 5235 become much more diffuse and at the higher temperatures could not be resolved at all. At 7°, however, the two bands were entirely separated. The blue and yellow bands are very slightly affected by temperature within the ranges investigated.

PRASEODYMIUM NITRATE.

A spectrogram (Plate 32, *A*) showing the effect of rise in temperature was made for a 2.6 normal aqueous solution of praseodymium nitrate 46.5 mm. deep. The exposures were made to the Nernst glower (current 0.8

ampere and slit-width 0.20 mm.) for 20 seconds. The length of exposure to the spark was 4 minutes. Starting with the strip nearest the comparison scale, the temperatures were 6°, 19°, 47°, 70° and 90°.

On account of the great concentration and the depth of cell, the absorption bands are very wide. The whole ultra-violet portion of the spectrum is absorbed up to λ 3550. Rise in temperature does not cause any change in this absorption. The band in the blue extends from λ 4300 to λ 4940 at 6°. A weak and rather broad band appears at λ 5120 and a narrow band at λ 5240, this band being about 15 Ångström units wide. The yellow band extends from λ 5760 to λ 6120 at 6°.

As the temperature rises the blue and yellow bands gradually widen. At 47° the blue band extends from λ 4290 to λ 4950, the yellow band from λ 5750 to λ 6120. At 90° the violet band was bounded by λλ 4280 and 4960, the yellow band by λλ 5740 and 6140. At 70° the ballast burned and the exposure to the Nernst glower was not quite as long as it should have been.

The bands λλ 5120 and 5240 appeared very slightly affected by the rise in temperature here used. The violet and yellow bands broadened very slightly and symmetrically with rise in temperature.

Plate 33, *A*, represents the absorption spectra of a 2.6 normal solution of praseodymium nitrate 3 mm. deep. Starting with the strip nearest the numbered scale, the temperatures are 6°, 16°, 34°, 46°, 58°, 70°, and 82°.

The four characteristic wide absorption bands appear very slightly affected by rise in temperature. The NO_3 band in the ultra-violet widens slightly.

CHAPTER X.

NEODYMIUM SALTS.

Introduction.—Neodymium salts in aqueous solutions.—Neodymium salts in glycerol.—Neodymium nitrate in nitric acid.—Spectrophotography of the chemical reactions in which neodymium salts take part.—Summary.

INTRODUCTION.

J. Becquerel has carried out investigations on several neodymium compounds similar to those on erbium. Tysonite was especially studied. This is a fluoride of cerium, lanthanum, and didymium and gives mainly the didymium spectrum. The bands λλ 5176^{++}, 5234^{++}, 6250 (doubles 4.5 unsym.), 6740, 6742^{+}, and 6760^{+} were found to broaden in the magnetic field. Employing the usual theory of the Zeeman effect, Becquerel shows that λ 3995 is due to + electrons; λ 5075^{+} to + electrons; λ 5109^{+} to − electrons; λ 5176^{++} to + electrons; λ 5234^{++} to − electrons, and λ 7642^{+} to − electrons.

At −180° the bands are much finer. The band λ 6249.7 is very fine and from the Zeeman effect it appears to be due to + and − electrons. The following table gives some of Becquerel's results:

Tysonite.			Parisite.		
λ at −188°.	$\Delta\lambda H = 15000$	$e/m = 2\pi v \dfrac{\Delta\lambda}{\lambda^2 H}$	λ at −188°.	$\Delta\lambda$	e/m
3996 *s*	0.8	+ 6.3 $(10)^7$	4274.8 *f*	0.20	− 1.38$(10)^7$
4259.8 *s* and *f*	0.1	− 0.7 $(10)^7$	4724.7 *f*	0.42	+ 2.37$(10)^7$
4268 *s* and *f*	0.1	+ 0.7 $(10)^7$	4747.0	0.40	− 2.20$(10)^7$
4721.4 *s* and *f*	0.1	− 0.6 $(10)^7$	5095.7 *s*	2.39	+11.56$(10)^7$
5064.4 *f*	0.4	+ 2.0 $(10)^7$	5186.0 *s*	0.37	+ 1.73$(10)^7$
5073.5 *f*	1.1	+ 5.32$(10)^7$	5208.0 *s*	0.37	− 1.71$(10)^7$
5079.1 *f*	0.54	− 2.63$(10)^7$	5220.0 *s*	0.18	+ 0.83$(10)^7$
5087.2 *f*	0.99	− 4.81$(10)^7$	5231.0 *s*	0.27	+ 1.24$(10)^7$
5098	0.33	+ 1.0 $(10)^7$	5256.0	0.60	− 2.70$(10)^7$
5110	0.92	− 4.4 $(10)^7$	5685.0	1.00	+ 3.90$(10)^7$
5173 *s*	0.53	+ 2.5 $(10)^7$	6232.7	0.77	− 2.40$(10)^7$
5185.7 *s* and *f*	0.27	+ 1.26$(10)^7$	6239.6	1.14	− 3.70$(10)^7$
5220 *s* and *f*	0.14	− 0.64$(10)^7$	6246.9	0.60	− 1.90$(10)^7$
5234.6 *s* and *f*	0.54	− 2.48$(10)^7$	6723.0	0.90	− 2.50$(10)^7$
6224.9 *f*	0.4	+ 1.2 $(10)^7$	6735.0	0.90	− 2.50$(10)^7$
6234.8 *f*	0.5	− 1.6 $(10)^7$	6746.0	0.90	− 2.50$(10)^7$
6242.6 *f*	1.2	− 3.90$(10)^7$			
6249.7 *s* and *f*	3.27	±10.52$(10)^7$			
6267 *f*	0.4	+ 1.30$(10)^7$			
6683	1.86	− 5.23$(10)^7$			
6740	0.86	− 2.38$(10)^7$			
6761	0.41	− 1.13$(10)^7$			

The series of acetate bands is very much like that of the uranyl series, The foregoing table shows that the Zeeman effect on related bands of tysonite and parisite is very different (parisite is a carbonate of the didymium group). An examination was made on yellow Spanish apatite, a flourphosphate of calcium and didymium. The apatite bands are quite broad. The band λ 5270 gave a circular vibration indicating + electrons, λ 5750 + electrons, λ 5820 + electrons, and λ 5860 – electrons.

A solution of neodymium nitrate in ethyl alcohol has also been tried. The bands $\lambda\lambda$ 5229, 5219, and 5239 were broken into two components by the magnetic field, the amount being 0.5 Ångström unit for $H = 14,000$ c.g.s. units. The sense of the polarization indicated – electrons. The bands $\lambda\lambda$ 5815 and 5831 are affected but little and indicate + electrons. The effect of the magnetic field seems to be independent of the solvent. The addition of perchloride of iron had no effect. The spectrum was observed as the solution was warmed so as to change the solid alcohol to liquid alcohol. No discontinuous change in the spectrum was noticed.

Neodymium chloride in alcohol (methyl) has a sensitive band at λ 5096 giving a separation of 1.1 Ångström units for $H = 14,000$. The sense indicates a + electron. λ 5207 gives a separation of 0.4 having a – sense, λ 5220 a separation of 0.4 in a – sense, while λ 5225 does not show any effect. The bands $\lambda\lambda$ 5761 (0.4, + electrons), 5787 (0.4, – electrons), 5796 (– electrons), and the two bands at 6800 (– electrons) gave measurable Zeeman effects. No difference was found between "water" and "alcohol" bands.

The addition of small amounts of the nitrate of neodymium to the chloride in an alcoholic solution rapidly causes the disappearance of the bands $\lambda\lambda$ 5207, 5225, 5727, 5745, and 5761. When equal amounts of the two salts are present these bands have practically disappeared. The band λ 5220 remains. At the same time new bands appear at $\lambda\lambda$ 5235, 5777, 5814, and 6229. The band λ 5229 is due to –, λ 5235 to –, and λ 5814 to + electrons.

Becquerel and Onnes[1] continued the work on absorption spectra at temperatures of liquid and solid hydrogen. The general effect of cooling is to make the bands more intense and often to cause new bands to appear. The reverse action very seldom occurs. But when the temperatures of liquid hydrogen (20° absolute) or solid hydrogen (14° absolute) are reached it is found that many bands have weakened, or even disappeared. The band λ 5235 of tysonite is a band of this kind. At very low temperatures, then, the spectrum is much simpler than at higher temperatures. Some of the bands even pass through a minimum of width. The band λ 5176 of tysonite passes through a minimum between 20° and 14°. Becquerel suggests that there should be a relation between the effect of temperature on the absorption and the effect of temperature[2] on electrical resistance. At very low temperatures the metals should be transparent.

The effect of a magnetic field on the absorption bands was found to be independent of the temperature, and this fact Becquerel believes is a strong argument for the view that positive electrons exist within the atoms.

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[1] Le Radium, Aug. (1908).

[2] Onnes: Comm. Leyden, suppl., 9, 25 (1904); Onnes and Clay: Comm. Leyden, 95, 99.

The following table gives the wave-lengths of the neodymium bands in aqueous solution as measured by various spectroscopists:

	Stahl.	Demarçay[1]	Muthmann.[2]	Drossbach.[3]	Foesling.[4]	Formanek.[5]	Exner.[6]
A	7420	7324	....	....	....	7291	....
B	6900	6910	6892	....	6895	6906	....
	6810	6804	6798	....	6775	6794	6750
	6710	6731	6720	....	6720	....	....
C	6360	6373	6360	....	6360	....	....
	6280	6292	6285	....	6278	....	....
	6240	....	6250	....	6254	6235	....
	6220	6234	6215	....	6217	....	....
D	....	....	5834	....	....	....	....
	....	....	5808	....	....	....	....
	5790	5783	5785	5880–5660	5788–5780	5797	5795
	5750	....	5754	....	5754	5759	5740
	....	....	5735	....	5735	....	....
	5720	....	5716	....	5716	....	....
E	5330	5320	5323	5320	5323	5319	5235
	5240	....	5254	5270–5190	....	....	....
	5210	5220	5216	....	5216	5222	....
	....	....	5205	....	5204	5209	....
	....	....	....	5160	......	....	5120
	5130	....	5120–5110	....	5124	5120	....
	5090	5109	5089	....	5087	5096	....
F	....	....	....	4780	4799	4821	4830
	4760	4768	4745	....	4748–4742	4759	4760
	4690	4691	....	4710	4687	4695	4700
	4620	4624	4595	4630	4610	4614	4620
G	....	....	....	....	....	4443	4430
	4340	4351	4340	4340	4330	4341	....
	4280	4294	4325	....	....	....	4270
	....	4281	4273	4275	4271	4271	....
	4190	4200	....	....	....	....	....
J	3800	....	3803	....	3804	....	....
K	3560	....	....	3590	....	....	....
	3540	....	....	3560	3538	....	3478
	3500	....	....	3510	3503	....	....
	3470	....	....	....	3468	....	....
L	....	....	....	....	3420	....	....
	3390	....	....	3370	....	....	....
	....	....	....	....	....	....	3350–3130
M	3290	....	....	3280	....	....	....

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[1] Compt. rend., **126**, 1039 (1898).

[2] Ber. d. deutsch. chem Gesell., **32** (1899).

[3] *Ibid.*, **35**, 486 (1909).

[4] Ztschr. anorg. Chem., **118** (1907).

[5] Die qualitat. Spectralanal. anorg. Körper, Berlin (1900).

[6] Wiener Sitzungsberichte, **118**, a 1252–1266 (1899).

Stahl states that the bands λ 6950, λ 6840, and λ 6780 vary enormously in their relative intensities in the various solutions. In the presence of strong nitric acid the bands λ 4710, λ 4690, and λ 4570 disappear completely. The absorption spectrum of the chloride is independent of the presence of free acid.

Neodymium: λ 6710, λ 6240, λ 5790, λ 5720, λ 4340, λ 4190, λ 3800, λ 3390, λ 3270.

Praseodymium: λ 5970, λ 5890, λ 4820, λ 4690, λ 4440.

The λ 4690 band is common to solutions of both neodymium and praseodymium, and this has led some to believe that there is a common element in these two substances. Stahl considers the view that there are several elements in neodymium as very improbable.

The Effect of Rise in Temperature on the Absorption Spectra of Aqueous Solutions of Neodymium Salts.

A spectrogram (Plate 38, *A*) of a 3.4 normal solution of neodymium chloride in water, 43 mm. deep, was taken. The exposures were made for 3 minutes to the Nernst glower, the current being 0.8 ampere and slit-width 0.20 mm. The time of exposure to the spark was 6 minutes. Starting with the strip nearest to the comparison spectrum, the temperatures were 6°, 21°, 36°, 47°, 60°, 77°, and 83°.

Neodymium chloride, under the conditions of this experiment, gives a complete absorption in the ultra-violet up to λ 3700. From λ 3700 throughout the violet and blue regions there is almost complete general absorption, this general absorption increasing with the temperature. A band of absorption seems to appear at about λ 4000, but this is somewhat doubtful. A very sharp and strong band appears at λ 4185. A band occurs at λ 4265 to λ 4305 and one at λ 4320 to λ 4350. The transmission band between these two bands is faint and disappears at 77°. An absorption band extends from λ 4380 to λ 4520 and there is then complete absorption up to λ 4980. The transmission between these bands is very weak and has almost disappeared at 83°. Between λ 4970 and λ 5365 there is an absorption band, the long wave-length edge of this band being extremely sharp. A similar band lies between λ 5620 and λ 6000. Next comes a series of five absorption bands. The first of these is 20 Ångström units wide and is at λ 6250, the next is 10 Ångström units wide and is at λ 6270. The bands λλ 6295 and 6315 almost touch each other, the distance between them being but two or three Ångström units. The last band is about 30 Ångström units in width and its center lies at λ 6380. The last band that could be photographed was between λ 6720 and λ 6965.

The effect of rise in temperature is quite evident, most of the bands widening and their sharpness gradually decreasing. At 83° the band λ 4970 to λ 5365 described above has widened to λ 4960 and λ 5395, the widening being slightly greater on the red side. The band λ 5620 to λ 6000 has widened to λλ 5610 and 6050, this widening also being unsymmetrical. The five bands in the vicinity of λ 5800 at 6° have merged into three bands. The red band is at λλ 6720 to 6990. It will thus be seen that the widening is in general greater on the red side of the bands.

A spectrogram (Plate 37, *A*) of the absorption spectrum as affected by change in temperature was made for a neodymium chloride solution in water, the concentration being 3.4 normal and the depth of layer 12 mm. The length of exposure was 2 minutes to the Nernst glower (current 0.8 ampere and slit-width 0.20 mm.). The time of exposure to the spark was 6 minutes. Starting with the strip nearest the numbered scale, the temperatures were 11°, 22°, 33°, 45°, 59°, 73°, and 85°.

At 11° an absorption band appears at about λ 2970, a very strong band from λ 3250 to λ 3285, and an adjacent band from λ 3285 to λ 3310. A very narrow and feeble transmission band separates these two bands. At 85° the transmission band has weakened very much. At 11° a very strong band lies between λ 3490 and λ 3580. The band λ 4274 is about 8 Ångström units wide. An extremely narrow band appears at λ 4297, λ 4306, and λ 4324. At λ 4234 is a wider and rather diffuse band, it being about 12 Ångström units wide. Bands lie between λ 4415 and λ 4470, λ 4580 and λ 4650, λ 4665 and λ 4710, λ 4740 and λ 4775, λ 4815 and λ 4835, and the very wide bands λλ 5010 and 5300 and λλ 5665 and 5935. Weak bands are located at λ 4645, λ 4800, λ 5320, λ 6235, λ 6255, λ 6280, λ 6305, and λ 6380. Rather diffuse bands appear at λλ 6780 and 6840, at λ 6850, and from λ 6870 to λ 6920.

The effect of rise in temperature from 11° to 85° is quite noticeable, although it is not great. In the ultra-violet there is a slight increase in the general absorption. The bands λλ 3285 and 3310 widen slightly. The band λλ 3490–3580 at 11° has widened so that at 85° it extends from λ 3450 to λ3600. The bands at λλ4415 and 4470 have widened but little. The bands from λ 4600 to λ 4800 have also widened but little. The faint diffuse bands λλ 4645 and 4800 have practically disappeared. The bands λλ 5010 and 5300 and λλ 5665 and 5935, at 11°, have widened at 85° to λλ 5010 and 5350 and λλ 5660 and 5985. The widening of the latter band is distinctly unsymmetrical. The existence of the band λ 5320 causes the band λ 5010 to λ 5300 to widen unsymmetrically.

The bands in the region λ 6300 become less sharp as the temperature rises. At 11° there was considerable transmission in the region λ 6850. At 85°, however, this transmission disappears and there is practically complete absorption from λ 6760 to λ 6920. The very sharp bands λλ 4282, 4300, 4310, 4322, and 4343 do not appear to change very much with change in temperature. On the strip taken at 73° these bands appear sharper than on any of the other strips.

A spectrogram (Plate 37, *B*) showing the effect of rise in temperature was made on a 0.17 normal neodymium chloride solution in water 196 mm. deep. The amount of neodymium chloride in the path of the light is approximately the same as in the spectrogram showing the effect of temperature on a 3.4 normal solution in a cell 12 mm. deep. In this case the temperatures were 5°, 16°, 28°, 42°, 59°, 72°, and 82°. Exposures were made to the Nernst glower for 3 minutes (current 0.8 ampere and slit-width 0.20 mm.). Each strip was exposed to the spark for 6 minutes. The purpose of making this spectrogram was to find the effect of concentration of a salt upon the changes produced by change in temperature.

A description of the bands at 5° and 82° will be given. Any change that takes place between these two temperatures is a gradual one. Transmission begins at λ 2600. Bands appear between λ 3250 and λ 3300 and λ 3455 and λ 3575. The band λ 4274 is much sharper and narrower than for the more concentrated solution. The numerous fine bands in the region λ 4300 are very faint. The bands λ 4420 to λ 4460, λ 4600 to λ 4630, λ 4645, λ 4680 to λ 4705, λ 4745 to λ 4770, and λ 4820 have rather diffuse edges. Wide bands appear from λ 5020 to λ 5290 and from λ 5685 to λ 5920. Diffuse bands are located at λ 5310, λ 6810, and λ 6900. The group in the region λ 6300 appears, but the bands are extremely faint.

At 82° the general absorption has increased in the ultra-violet and has reached to about λ 2800. It will be noticed here that the effect of rise in temperature upon this general ultra-violet absorption is greater for the dilute solution than for the concentrated solution which has been previously described.

The band λλ 3455 to 3575 at 5° has widened slightly, having the limits λλ 3445 and 3580 at 82°, the widening being about 15 Ångström units. This band in the concentrated solution widened 60 Ångström units. Practically no effect on the bands from λ 4200 to λ 4900 is to be noticed with rise in temperature. At the higher temperature the bands are slightly more diffuse, but this change is very small. The band λλ 5020 to 5290 at 5° has widened to λλ 5015 and 5285, about 10 Ångström units. The corresponding widening for the concentrated solution was approximately 50 Ångström units; although it must be noted that in the more concentrated solution this widening was mostly due to the increased absorption of the band λ 5310 at the higher temperatures. The band λ 5685 to λ 5920 at 5° has widened to λλ 5775 and 5930, about 20 Ångström units, compared with a widening of 55 Ångström units for the more concentrated solutions. None of the other bands show any appreciable change with change in temperature.

A spectrogram (Plate 39, *A*) was made showing the effect of temperature on the absorption spectrum of a 1.66 normal aqueous solution of neodymium bromide, the depth of layer being 6 mm. An exposure of 4 minutes was made to the Nernst glower (0.8 ampere and a slit-width of 0.20 mm.). The length of exposure to the spark was 6 minutes. The temperatures, starting with the strip adjacent to the comparison spectrum, were 4°, 20°, 36°, 50°, 68°, and 83°.

At 4° there is complete absorption in the ultra-violet up to λ 2600. A broad absorption band appears at λ 2660 to λ 2800 and from λ 2950 to λ 3060. These absorption bands appear with a more or less general absorption. Bands appear at λλ 3460, 3500, and 3540. The band at λ 4274 is weak. Weak and diffuse bands occur at λλ 4440, 4630, 4695, 4825, 5095, 5260, 6810, and 6900. Wider bands are located at λλ 5116 to 5140, λλ 5200 to 5240, and λλ 5710 to 5850.

At 83° the spectrum is almost exactly the same as at 4°. The ultra-violet absorption is complete up to λ 3050. The bands at λ 3500 have increased in width slightly and the band λ 4274 is slightly broader. The bands that have widened appreciably are λλ 5195 to 5260 and λλ 5700 to 5880. The change in the absorption is greater when the temperature is changed from 68° to 83°. Up to 68° there is practically no change in the absorption spectrum at all.

A spectrogram (Plate 39, *B*) showing the effect of temperature was made, using a 0.055 normal aqueous solution of neodymium bromide, the depth of layer being 197.4 mm. This spectrogram was made for comparison with that for a 1.66 normal solution of the same salt 6 mm. deep. The exposures to the Nernst glower lasted 90 seconds in this case (current 0.8 ampere and slit-width 0.20 mm.). The length of exposure to the spark was 6 minutes. Starting with the strip nearest to the comparison scale, the temperatures of the solution were 5°, 16°, 29°, 42°, 55°, 68°, and 84°.

At 5° there is practically complete transmission of light between λ 3400 and λ 2600, no ultra-violet bands appearing, as was the case for the more concentrated solution. The bands λλ 4445, 4693, 4760, 4825, and 5095 were somewhat sharper than they were in the concentrated solutions. The two largest bands extended from λ 5200 to λ 5250 and from λ 5710 to λ 5850. As in the case of the more concentrated solution, so here, the greatest change in the absorption took place in the change from 68° to 84°. The ultra-violet absorption increased up to λ 2900. The bands at λ 3500 became considerably stronger, but they widened very little. The bands λλ 4445, 4693, 4760, and 4825 are somewhat weaker than at 5°. The wide bands remained practically as wide as at 5°, λ 5200 to λ 5250 and λ 5705 to 5870. This indicates a widening of about 25 Ångström units for the latter band. For the more concentrated solution the widening of these two bands was 25 and 40 Ångström units, respectively. It is thus seen that in the more concentrated solutions the bands widen more with rise in temperature than they do in the less concentrated solutions. At 42° in the dilute solution there appears a narrow band at λ 6710. This increases in intensity with rise in temperature. This band does not appear at all in the concentrated solution.

A spectrogram (Plate 40, *A*) was made of neodymium chloride and calcium chloride in water. Exposures were made for 30 seconds to the Nernst glower, the current being 0.8 ampere and the slit-width 0.20 mm. The length of exposure to the spark was 4 minutes. Starting with the strip nearest the numbered scale, the temperatures were 6°, 17°, 31°, 49°, 63°, 74°, and 82°.

The general effect of the addition of calcium chloride is to make all the bands hazier, and to increase the transmission throughout the region of the band. At 6° there is a slight transmission throughout the ultra-violet portion of the spectrum. As the temperature is raised this general transmission is decreased, and at 82° practically no light of shorter wave-length than λ 2800 passes through the solution. Sharp bands occur at λ 3464, λ 3500, λ 3535, λ 4276 and weak diffuse bands at λ 4295, λ 4305, λ 4340, λ 4445, λ 4620, λ 4695, λ 4760, λ 4825, λ 5095, λ 5130, λ 5225, λ 5260, λ 5320, λ 5710 to λ 5860, λ 6245, λ 6810, and λ 6900.

At 82° the bands in the λ 3500 region are slightly more intense than at 6°. Practically all the bands from λ 4200 to λ 5200 have become much weaker at the higher temperature. This is especially true of the band λ 4276, its intensity being less than half what it is at 6°. Most of the bands are shifted to the red with reference to the same bands at 6°. For instance, λ 5095 is shifted 5 Ångström units towards the red. The bands λ 4695, λ 4760, and λ 4825 are all shifted to the red at the higher temperature, and especially λ 4825, the shift in this case amounting to 5 Ångström units. In the case of these bands the shift is not an apparent one due to unsymmetrical broadening, for in this instance there is no broadening at all.

The band from λ 5710 to λ 5860 at 6° has widened very unsymmetrically and has the limits λ 5710 to λ 5920. The short wave-length side is quite sharp and its position is practically independent of the temperature. The long wave-length edge is quite broad and recedes quite rapidly towards the red as the temperature is raised. The bands in the red, λλ 6810 and

6900, grow fainter and fainter with rise in temperature, and have practically disappeared at 82°. The band λ 6245 is very weak at 6° and has disappeared at about 60°.

It will thus be seen that not only does the presence of calcium chloride modify greatly the absorption of neodymium chloride, but that it changes the effects due to temperature very fundamentally. In pure neodymium chloride practically no bands decrease in intensity with rise in temperature, and at present no shift has been detected. When calcium chloride is added to the solution most of the bands decrease in intensity with rise in temperature and several are shifted towards the red at the same time. Several bands disappear. Moreover, although the band λλ 6800 to 6900 widens, this widening is entirely on the red side, whereas for the pure neodymium chloride solution this widening always takes place on both sides of the band.

A spectrogram (Plate 40, *B*) was made to show the effect of change in temperature on a 2.15 normal aqueous solution of neodymium nitrate. The length of layer was 3 mm. The exposures were for 40 seconds to the Nernst glower (current 0.8 ampere, slit-width 0.20 mm.). The length of exposure to the spark was 6 minutes. Starting with the strip nearest the comparison spectrum, the temperatures recorded were 4°, 17°, 29°, 43°, 58°, 71°, and 84°.

The changes in the spectrum due to this change in temperature of 80° were very slight. The NO_3 band extends to about λ 3250 at 4°, and to about λ 3280 at 84°. The bands at λ 3500 became considerably wider and their edges more diffuse at the higher temperatures. At the lower temperatures fine bands appear at λλ 5210, 5225, and 5240. At 84° these bands all merge into a single band. The red band extends from λ 5705 to λ 5860 at 4°. The band at λ 5820 is very faint at the lower temperatures. At 84° it is unrecognizable. At this temperature the red band extends from λ 5700 to λ 5880. The widening of this band for the concentrated solution is somewhat greater than for the dilute solution, but the effect of concentration is very slight. This is to be expected since the effect of temperature itself is so very minute.

A spectrogram was made of a 1.66 normal aqueous solution of neodymium bromide 54.6 mm. deep. The exposures were 3 minutes to the Nernst glower and 6 minutes to the spark. The current in the Nernst glower was 0.8 ampere and the slit-width 0.20 mm. Starting with the strip nearest the comparison scale, the temperatures were 6°, 20°, 33°, 47°, 62°, 73°, and 82°.

The effect of rise in temperature on the absorption spectra of this salt was quite marked, practically all of the bands broadening and becoming more intense. At 6° the ultra-violet absorption extended to λ 3600. At 82° it had advanced to λ 3800. Very narrow and fine bands appear at λλ 4186, 4300, 4308, 4345, 6240, 6265, 6290, 6305, and much broader bands at λ 6380 and λ 6740. Wide bands occur from λλ 4390 to 4480, λλ 4550 to 4850, λλ 4990 to 5340, λλ 5650 to 5950, and λλ 6760 to 6930, at 6°. At 82° these bands have the following limits, respectively: λλ 4380 to 4500, λλ 4540 to 4910, λλ 4960 to 5370, λλ 5620 to 5990, and λλ 6730 to 6960.

A spectrogram (Plate 38, *B*) was made of a 2.96 normal aqueous solution of neodymium nitrate 38.5 cm. deep. An exposure of 3 minutes was made to the Nernst glower, the current being 0.8 ampere and the slit-width 0.20 mm. The length of exposure to the spark was 6 minutes. Starting with the strip nearest the comparison scale the temperatures were 7°, 17°, 30°, 44°, 59°, 70°, and 82°.

At 7° there is practically complete absorption in the ultra-violet up to λ 4600, due to the absorption of the NO_3 group. The edge of the band is very sharp. Other bands are as follows: λ 4270 to λ 4288, λ 4386 to λ 4500, λ 4538 to λ 4870, λ 4970 to λ 5370, λ 5620 to λ 6005, λ 6240 to λ 6270, and λ 6705 to λ 6970.

It should be noticed here that the absorption spectrum of neodymium nitrate under the present conditions is quite different from the absorption of a similar solution of neodymium chloride. In the case of the chloride there was a very great amount of absorption throughout the ultra-violet and violet portions of the spectrum. In the case of the nitrate there is almost complete absorption up to λ 3600 and from that wave-length to λ 4270 there is complete transmission. In this region appeared several narrow and sharp bands in the neodymium chloride absorption spectrum.

From the spectrum shown in the upper strip and for which the temperature was 82° we see that the NO_3 band extends to λ 3615. The band λ 4274 has become about 5 Ångström units wider than it was at 7°. A wide and weak band appears at λ 4350, and this is considerably stronger than at the lower temperatures. The positions of the other bands are: λ 4380 to λ 4560, λ 4535 to λ 4870, λ 4970 to λ 5390, λ 5615 to λ 6025, and λ 6700 to λ 6970. The increase in width of these bands due to raising the temperature from 7° to 82°, is 60, 20, 25, and about 0 Ångström units, respectively.

A spectrogram was made of the absorption spectra of a 2.15 normal solution of neodymium nitrate 3 mm. deep. Starting with the strip nearest the numbered scale, the temperatures were 4°, 17°, 29°, 44°, 58°, 71°, and 84°.

As the temperature rises the NO_3 band widens slightly. The bands in the region of λ 3500 become more diffuse and slightly wider. The same is true of the bands at λ 5200. The broad band at λ 5800 widens, especially on the long wave-length edge.

A spectrogram (Plate 40, *B*) was made of a very dilute solution of neodymium nitrate in aqueous solution of 0.036 normal concentration and 197 mm. depth of cell. The length of exposure to the Nernst glower was 20 seconds, current being 0.8 and slit-width 0.20 mm. The length of exposure to the spark was 5 minutes. Starting with the strip nearest the comparison spark-spectrum, the temperatures were 9°, 22°, 42°, 56°, 69°, and 78°.

The effect of temperature on the absorption of neodymium at this concentration is very slight. At 9° there is almost complete absorption up to λ 3300, due to the NO_3 band. Bands are located at λ 3460, λ 3500, λ 3530, λ 4273 (weak), λ 4445, λ 4610, λ 4692, λ 4756, λ 4820, λ 5093, λ 5136, λ 5197 to λ 5247, λ 5255, λ 5330, λ 5705 to λ 5860, λ 6800 and λ 6900.

At 78° the NO_3 has advanced about 30 Ångström units towards the red. The bands in the region of λ 3500 have widened slightly. The intensities of the other bands have changed but little. The wide band in the red extends from λ 5705 to λ 5875, there being a slight widening on the long wave-length edge of the band. The bands λ 6800 and λ 6900 are slightly more diffuse than at 9°, but this change is very small. The bands from λ 4200 to λ 5000 seem to be slightly shifted towards the red at the higher temperatures. In all, this shift, however, is not greater than 2 or 3 Ångström units.

Neodymium Salts in Glycerol.

A run was made to test whether Beer's law holds for glycerol solutions. Plate 35, *A*, represents a spectrogram ranging from 0.84 to 0.105 normal, the amount of absorbing matter being kept constant. The more dilute solutions show greater general absorption in the ultra-violet. Otherwise Beer's law is found to hold.

Plate 43, *A*, is the spectrogram of a solution of neodymium chloride in glycerol taken in the silica cell at various temperatures. The plate shows a slight widening of the bands, but this is very small. Some of the finer bands indicate a slight shift towards the red with rise in temperature. This, however, is quite small and never amounts to more than 3 or 4 Ångström units for any band.

Plate 46, *A*, shows the effect of rise in temperature of solutions containing neodymium and aluminium or calcium chlorides in glycerol. In the third and fourth strips it is to be noticed that the wide band at λ 5800 is shifted slightly to the red. The band at about λ 4295 seems to be shifted 2 or 3 Ångström units to the red. The shift is very small and is obscured in part by the increased diffuseness of the bands at the higher temperature.

Plate 29, *B*, represents the effect of rise in temperature on the absorption spectra of pure neodymium chloride in glycerol. The shift of the bands in this case can hardly be noticed. The effect of the presence of calcium is to cause the temperature shift of the bands to be increased. The effect is not as great as it is in aqueous solutions.

The absorption spectrum of neodymium chloride (Plate 34, *A* and *B*) in glycerol is very similar to that of an aqueous solution. The ultra-violet bands λλ 3475 and 3550 are quite strong and sharp. A weak band appears at λ 3520. For the 3 mm. depth of cell and smallest concentration the following bands appear: λλ 4290 (weak), 4710 (very weak), 5120 (wide, hazy, and apparently a triplet), 5230, 5240 (strong and fairly sharp), 5250, 5270 (weak and fuzzy), 5740 (wide and hazy), 5790, 5805, 5820, and 5850. The latter three bands practically merge into a single band, the transmission between them being very weak.

The greatest concentration and the 9 mm. depth of cell (upper strip of Plate 34, *A*) shows several additional bands: λλ 3600, 4190 (very diffuse), 4288, and two very fine components at 4270 and 4305, 4330, 4345, 4365, a wide (50 Ångström units) band at 4460, and similar but weaker bands at 4620, 4840, 5340, 5940, 6240, 6265, 6400, 6800, with narrower and sharper bands at 4710, 4730, 4760, 4790, 5170, and 5190.

The "glycerol" bands are very similar to the "water" bands but are all of slightly greater wave-length. The sharp "water" band at λ 4274 is composed of three bands in the glycerol solution. The "glycerol" bands are quite persistent and for a solution containing 10 per cent water the bands are practically "glycerol" bands. In general, the "water" and "glycerol" bands are so close to one another that we can not tell whether both bands coexist when the neodymium salt is dissolved in a mixture of the solvents. But the λ 4288 band apparently shifts gradually into the λ 4274 "water" band. No sign of the two bands coexisting is to be seen.

Neodymium Nitrate in Nitric Acid.

Plate 42, *B*, gives the absorption spectra of neodymium nitrate in nitric acid. The effect of free nitric acid is very pronounced. All the bands are wide and diffuse and differ very much from the absorption when there is no free acid. The first band to appear is λ 5830 and it appears as a very faint diffuse band. Then come the bands λλ 3470, 3520, 3550, 5130, 5250, 5730, 5970, and for a greater depth of cell λλ 4280, 4310, 4340, 4360, 4390 to 4460, 4480, 4600, 4650 (weak), 4705 (strong), 4745 (strong), 4840, 5385 (strong), 6245, 6275, and 6770.

In general, it has been shown that the presence of nitric acid is to shift the uranyl and uranous bands to the violet. This does not seem to be the effect of adding a large amount of acid to neodymium nitrate in aqueous solution. Many of the above bands do not seem to be bodily shifted to the red, but, like the band marked λ 4280, they are widened on the red side. The narrow band λ 4274 of the neutral nitrate lies within the broad and diffuse band λ 4280. As will be remembered, the action of free nitric acid on the uranyl nitrate bands was to cause them to become sharper. At the same time the bands were shifted to the violet.

Some of the bands that Stahl considered as absent in the presence of nitric acid appear on our plates, the band λ 4705 above apparently being his bands λλ 4690 and 4710.

SPECTROPHOTOGRAPHY OF CHEMICAL REACTIONS.

During the progress of the work quite a number of photographs were made of a salt in mixtures of two solvents. It seemed of interest to photograph the absorption spectra of a salt when different amounts of an acid were added to the given salt in solution. *In the case of uranyl salts several were found to have different absorption spectra.* In the case of neodymium, however, it was found that the various salts had practically the same absorption spectra. The absorption of the acetate was, however, found to differ from that of the other salts, so that the chemical changes produced by adding various acids were photographed with the aid of the spectroscope.

Plate 41, *B*, represents the absorption spectra of an aqueous solution of neodymium acetate, the concentration being kept constant and only the depth of cell being changed.

It will be seen from a mere glance that the absorption spectra of the acetate is quite different from that of the other neodymium salts. All the bands are much wider and less intense. Many of the broad bands that appear as several finer bands in the spectra of the other salts, appear here as single and very weak when the depth of cell is small.

The following are the wave-lengths of a few of the bands: λλ 3485, 3520, 3820, 4040, 4200, 4295, 4333, 4360, 4460, 4630, 4720, 4770, 4850, 5140 (very wide and weak), 5260, 5360, 5660, 5800 to 5860, 6820, and 6950.

It will be noticed that all the bands are 10 to 20 Ångström units farther to the red than the corresponding bands of the other neodymium salts.

The *A* section of Plate 41 represents the effect of adding nitric acid to a solution of neodymium acetate. The first strip of *A* contains nitric acid and shows that the acetate bands have been shifted some 10 Ångström units towards the violet by this addition of acid. This shift occurs before any other change of the acetate bands takes place.

Plate 41, *A*, represents a spectrophotograph of the effect of adding nitric acid to an aqueous solution of neodymium acetate. The addition of nitric acid causes the absorption in the ultra-violet to increase. The general effect on the neodymium bands is to cause the bands to become sharper, and, then, as more and more acid is added, to make the bands diffuse again. When the bands are sharpest they are practically the same as the bands of neodymium nitrate in water. It requires the addition of a very considerable amount of nitric acid to produce the nitrate neodymium bands. A description of the plate is to be found on page 150.

The group of bands in the region λ 3500 in the first and seventh strips appear to be slightly displaced to the red. In fact, all the " nitrate " bands of the third and fourth strips are some 10 Ångström units farther towards the violet than the bands of the first and seventh strips.

Strip 1.	Strip 3.	Strip 7.
3470	3465	3470
3510 very fuzzy	3505	3515 very fuzzy
3550	3533 sharp	3550
4285	3553	4285
4705	4275	4705
	4695	

In strip 1 there is a strong band at λ 5230 to λ 5250. In strip 2 appears a very fine and weak band on the shorter wave-length side of the wide band at λ 5240. In strips 3 and 4 the two bands are of equal intensity and are located at λ 5225 and λ 5234. In strip 5 a band appears on the red side of λ 5234. At the same time λ 5234 has become very much stronger than λ 5225. In strip 7 λ 5225 has become very weak. In strip 7 there are weak and fine bands at λ 5205, 5225 and a band from λ 5230 to λ 5250.

The group of bands at λ 5800 behave in the same way. In strip 4 there are bands at λλ 5730, 5755, 5775, 5800, and 5820. In strip 1 is a hazy band at λ 5750 and others at λλ 5790, 5820, and 5870. In strip 7 there are four bands, two at λ 5730 to 5760 and two at λ 5770 to 5830. The bands λλ 6800, 7040, and 7100 appear only in the central strips.

A spectrogram was made to show the coexistence of the " water " and " alcohol " bands of neodymium chloride. The spectrogram is shown as Plate 43, *A*. Anhydrous neodymium chloride was dissolved in a solution containing 8 per cent water and 92 per cent ethyl alcohol. The first four strips represent a Beer's law run, the concentrations being 0.5, 0.3, 0.1, and 0.05 normal, the most concentrated solution being the one whose spectrum is next to the scale. The last three strips represent a constant concentration where the depth of cell is increased.

The spectrogram shows that Beer's law does not hold, the more concentrated solutions being the greater absorbers. This is especially true of the alcoholic portion of the absorption. In strip 1 the " alcoholic " band corresponding to the " water " band λ 4274 has about the same intensity as the " water " band. In strip 4, however, the " alcohol " band has become very weak, indeed, while the water-band has slightly increased in absolute intensity as compared with strip 1. Several other bands indicate the same change. The " alcohol " bands thus weaken in intensity as the concentration is decreased, while the " water " bands do not.

In this connection experiments are now in progress in which it will be tested whether changes in temperature, the addition of chemical reagents, etc., affect the different bands in the same way.

Plate 43, *B*, represents the effect of adding hydrobromic acid to an aqueous solution of neodymium acetate. The first strip represents the absorption of a solution of neodymium acetate in water to which about a drop of hydrobromic acid has been added. Strip 2 represents the same to which several more drops of hydrobromic acid have been added. The remaining strips represent the absorption of the same solution to which more and more hydrobromic has been added.

The first strip gives the characteristic acetate spectrum. In order to give the effect of the acid the wave-lengths of the bands of the acetate measured on the film itself are given and compared with the spectrum of strip 2.

Strip 1.	Strip 2.	Strip 1.	Strip 2.
....	3465	4800 to 5150 gen. absorp.	4830
....	3510		5105
....	3543		5140
....	3560	5240	5225
4290	4285		5240
4450	4445	5745	5740
	4460	5760	5760
4715	4705	....	5775
4775	4775	5790	....
		5825	5810
		5870	....

The effect of adding a very small amount of hydrobromic acid is very pronounced. The addition of larger amounts of hydrobromic acid has very little effect. The shifting effect of hydrobromic acid is very small as compared with the same effect produced by nitric acid on the nitrate. The presence of a large amount of hydrobromic acid does not make the bands hazy and wide.

Plate 44, *A*, represents the effect of adding hydrochloric acid to an aqueous solution of neodymium acetate. The first strip represents the absorption of the pure aqueous solution of the acetate. The second strip represents the absorption of the same to which one drop of hydrochloric acid has been added. The third strip represents the absorption of the solution to which two more drops of acid have been added. The acid used was concentrated. The following table represents in part the changes which the addition of acid has caused to take place.

It will be seen that the addition of but a small amount of acid caused the appearance of a large number of fine bands, especially in the region of λ 5800. It also caused a very considerable shift of all the bands to the violet, an action similar to that of nitric acid. Further addition of acid brought out a spectrum very similar to that of neodymium chloride as shown by strips 3 and 4. Still further addition of acid produces other changes, one being the appearance of new bands in the region λ 5900.

Plate 45, *A*, gives a spectrogram where known amounts of hydrochloric acid were added to an aqueous solution of neodymium acetate.

Strip 1.	Strip 2.	Strip 3.	Strip 6.
3485 3530 3560	3465 3510 3540 3560	3465(s) 3510 3540 s 3560 3580	The whole group is very weak and diffuse
4297	4285	4285	4285 very weak 5305 very weak 5350 very weak
	4710 4775 4845	4710 4775 4845	
5140	5110 5140	....	
5260	5225 5245 5235	5230 s 5245 s	5230 very weak 5245 very weak
5760 5810 5850	5740 5760 5780 5795 5815 5830 5865 5870 5895 5910	5740 5760 5780 5810	5750 5785 .... 5815 5900 5930

A spectrogram (Plate 44, *B*) was made of mixtures in various proportions of neodymium acetate and neodymium chloride in water. Strip 1 is the pure acetate and strip 7 the pure chloride. The intermediate strip represents mixtures, the amount of chloride increasing from the bottom upwards. The concentration of neodymium was kept constant.

From this spectrogram evidence is obtained that each of the two salts has its own spectrum. As the amount of acetate is decreased the acetate bands gradually decrease in intensity and finally disappear. At the same time the chloride bands increase in intensity.

The band λ 5225 apparently is a chloride band, and does not appear in the acetate solution. On the other hand, the band λ 5830 and the very diffuse band λ 5860 appear to be acetate bands, and gradually disappear as the amount of acetate decreases.

A question which was raised by a study of some of the other spectrograms was whether by the addition of hydrochloric acid to the acetate different chemical compounds were formed. In the above spectrogram only two sets of bands appear, and it thus seems very probable that when hydrochloric acid is added to the acetate more than two compounds exist, for there are more than two sets of bands. Indeed, it seems probable that there is *a whole series of compounds or systems formed between the acetate on the one hand and the chloride on the other.*

Plate 45, *B*, represents the effect of adding hydrochloric acid to an aqueous solution of neodymium citrate. The absorption spectrum of the citrate is very similar to that of the acetate, and the changes in the absorption spectra are very similar to those that take place when mixtures of the acetate and chloride are dissolved in water. In other words, there are bands here: " citrate " bands which are very similar to the " acetate " bands. As hydrochloric acid is added the characteristic " citrate " bands gradually decrease in intensity while the "chloride " bands increase in intensity. There is no evidence here of more than two chemical compounds.

SUMMARY.

No salts show the complexity of absorption spectra better than those of neodymium and erbium. Some of the bands are wide and diffuse, some narrow and strong—in fact bands of very great diversity of appearance are present. In any given solvent the absorption spectra of the various salts are very similar and in many cases practically identical. But when the solutions are very concentrated or when the salts themselves are investigated, it is found that the absorption spectra are entirely different for each salt. The fact that the absorption of different salts in the same solvent is very similar is a strong argument *that the solvent plays a very important rôle in the absorption of light.* This view is very much strengthened when it is found that the absorption in different solvents is different, and that in mixtures of solvents both solvent bands coexist.

During the work on the absorption of uranyl nitrate to which sulphuric acid was added, the very fine banded absorption spectra of nitric oxide were obtained. From the conditions of the experiment it seems very probable that this nitric oxide was in solution. Granting that this is the case, the experiment shows that the solvent itself under some conditions may not have any effect upon the absorption spectra. It seems reasonable to suppose that it is when chemical combination between solvent and solute takes place that the absorption of light is greatly modified.

In the case of neodymium bands it is very difficult to change the wave-length of the bands. Becquerel and others show that there are small changes as the neodymium is cooled to very low temperatures. The absorption spectra of salts at 600° indicate but slight changes in wave-length compared with the salts at 0°. For some bands the shift is about 10 Ångström units. Our work shows practically no shift in the absorption bands of pure aqueous solutions between 0° and 90° C. However, when calcium or aluminium is present, in some cases there are shifts.

The absorption spectra of neodymium chloride have been photographed in glycerol and alcohol solutions. There are indications of alcohol- and glycerol-bands. The latter are more persistent than the alcohol-bands. In the case of glycerol there seemed to be one band that gradually shifted from the water to the glycerol position, indicating the possibility of the existence of intermediate glycerolates.

The effect of free nitric acid on the bands of neodymium nitrate is to cause them to become much broader and more diffuse than the bands of the neutral salt. Some of the bands are caused to broaden more on the red than on the violet side. The effect of free nitric acid on the neodymium bands is thus very different from the effect on the uranyl nitrate bands.

Early in the work it was intended to alter conditions so that each band could be followed throughout the various changes that it underwent. In most cases, however, this is at present very difficult to do, on account of the very sudden changes in the character of the spectra, and in many cases also on account of the diffuseness of the bands. For instance, the band λ 4274 is certainly one of the most characteristic bands of the water-spectrum. In glycerol it is found that apparently this band gradually shifts to λ 4288 for a pure glycerol solution. For solutions containing a large amount there appear fine satellites at λ 4270 and λ 4305. In alcohol the band appears at λ 4290. The band λ 4274 does not, however, shift into the alcohol-band. In a solution of neodymium nitrate in water as made by Anderson there appear two strong bands close together, the distance between the opposite edges being about 10 Ångström units, and between the adjacent edges, 2 Ångström units. Neodymium nitrate and sulphate crystals each give two strong components, but in this case the distance between the opposite edges is 15 Ångström units, and between the adjacent edges 6 Ångström units. In other words, in the neodymium nitrate crystal the components are farther apart than in the nitrate solution as made by Anderson. In the solutions made by Jones only one component appears. A remarkable result manifests itself when the water of crystallization of the sulphate and nitrate crystals is driven off. The rather paradoxical effect is to cause the "λ 4274" bands to become weaker and appear as a single band. In the case of neodymium nitrate, driving off the water of crystallization causes many of the bands to be shifted towards the red. For the sulphate the drying results in a shift of some bands to the violet, while other bands remain unshifted. The dry nitrate bands in several photographs made by Anderson are all of some 50 Ångström units greater wave-length than the dry chloride, dry sulphate, or crystal sulphate bands. It is at present premature to attempt to interpret these changes, since the intermediate steps have not been followed. Much work remains to be done in this direction.

In aqueous solutions it has been found that the absorption of neodymium acetate is different from that of the chloride, bromide, and nitrate. By adding inorganic acids to the acetate, photographs have been made of the spectrum, as the acetate was changed to another salt. These spectra indicate that *in some of the reactions there probably exist several systems or compounds between the acetate and the salt of the acid added.*

CHAPTER XI.

URANIUM SALTS.

Absorption spectra of uranium compounds.—Absorption spectra of uranyl chloride.—Absorption spectra of uranyl nitrate.—Absorption spectra of uranyl bromide, sulphate, and acetate.—Spectrophotography of the chemical reactions of uranyl salts; conductivity data.—The phosphorescent and fluorescent spectra.—Absorption spectra of uranous salts.

THE ABSORPTION SPECTRA OF URANIUM COMPOUNDS.

There are quite a large number of spectra of the various compounds and decomposition products of the element uranium. The absorption spectra consist chiefly of the banded spectra of the uranyl and uranous compounds. Uranyl salts in solution are yellow and their absorption spectra consist of a broad band of general absorption in the ultra-violet, which extends more and more into the region of longer wave-lengths as the amount of uranyl salt solution in the beam of light is increased. The edge of this absorption band as it gradually advances through the violet and into the blue shows several diffuse bands about 50 Ångström units wide and about 100 Ångström units distant from each other. These comparatively fine bands, about twelve in number, are weak, having very diffuse edges, and can be photographed only when they lie near the edge of the general absorption band. Among those who have carried out investigations upon the absorption spectra of these compounds may be mentioned: H. Oeffinger,[1] H. Becquerel,[2] W. Boehlendorff,[3] O. Knoblauch,[4] E. Deussen,[5] Formánek,[6] Hartley,[7] Houstoun and Russel,[8] Jones and Strong,[9] Strong,[10] and others.

In the discussion of the uranyl bands it will be found convenient to designate them by the letters *a*, *b*, *c*, *d*, etc., the band *a* being of the greatest wave-length, and the wave-lengths of the other bands gradually decreasing. In general it will be found that this classification is very useful, and upon general observations it might be supposed that each band had its origin in a particular vibration of the vibrating system. But at low temperatures these bands are found to consist of a number of much finer bands, and the absorption spectra become very complicated indeed, so that it is clear that changes which are observed at ordinary temperatures may be due to relative changes in the groups of five bands composing the larger bands,

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[1] Ueber die Lichtabsorption der Uransalze, Inaug. Diss., Tübingen, 1866.
[2] Ann. Chim. Phys., (6) **14**, 170–257 (1888).
[3] Inaug. Diss., Erlangen, 1890.
[4] Wied. Ann., **43**, 738–783 (1891).
[5] *Ibid.*, **66**, 1128–1148 (1898).
[6] Die qualitative Spectralanalyse anorg. Körper, Berlin, 1900.
[7] J. Chem. Soc., **83**, 221–246 (1903).
[8] Proc. Roy. Soc. Edinb., **29**, II, 68.
[9] Phys. Zeit., **10**, 499 (1909).
[10] Phys. Rev., **29**, 555 (1909); **30**, 279 (1910).

a, *b*, *c*, *d*, etc. For instance, shifts in the position of the bands, *a*, *b*, *c*, etc., due to relative changes in the intensity of the components, may be observed when the frequency of none of the component bands has been changed at all.

Becquerel[1] found that the position and intensity of the absorption bands of a crystal depend on the direction in which the light traversed the crystal. To study this phenomenon of absorption he cut sections of crystals in three different directions. One section was cut parallel to the optic axes that cut each other obliquely ("axe moyen"), one section perpendicular to the bisector of the acute angle (" bissectrice aiguë"), and another section perpendicular to the bisector of the obtuse angle (" bissectrice obtuse"). Crystals of uranyl nitrate belong to the orthorhombic type. Becquerel measured the wave-lengths of the three bands, *a*, *b*, *c*, for the different sections.

URANYL NITRATE.

	a.	*b*.	*c*.
Bissectrice aiguë...........	λ 4870 to λ 4840	λ 4725 to λ 4666	λ 4568 to λ 4525
Axe moyen................	....	λ 4698 to λ 4660	λ 4555 to λ 4520
Bissectrice obtuse..........	λ 4864	λ 4695	λ 4551

The wave-lengths of the absorption bands of crystals of the double chloride of uranyl and potassium were as follows:

Bissectrice aiguë...........	....	λ 5007	λ 4905	λ 4957
Axe moyen................	....	λ 5000	λ 4935 to λ 4920	....
Bissectrice obtuse..........	λ 5047	λ 5000	λ 4953 to λ 4910	....

Bissectrice aiguë...........	....	λ 4843	λ 4783	λ 4741	....
Axe moyen................	λ 4869	....	....	λ 4741	λ 4702
Bissectrice obtuse..........	λ 4869	λ 4826	λ 4783	λ 4741	λ 4702

Knoblauch[1] investigated the effect of change of concentration on the absorption spectra of various uranyl salts. He kept the amount of salt in the path of the beam of light constant but varied the concentration between wide limits. In the case of uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, he compared the absorption of solutions having concentrations about 1.1 normal (c_1) and 0.0033 normal (c_2) ($c_1 : c_2 = 3428 : 1$). If the molecules of uranyl nitrate had acted like the molecules of a gas, the concentrated solution would have exerted a pressure of 25.4 atmospheres and the dilute solution $\frac{1}{136}$ atmosphere. For both solutions the *a* (λ 4920–4850) and the *b* (λ 4780–4680) bands appeared in the same position. With uranyl acetate, $UO_2(C_2H_3O_2)_2 2H_2O$, a change in concentration of $c_1 : c_2 = 446 : 1$ did not cause any shift in the *a* (λ 4940–4870) or the *b* (λ 4820–4730) bands. The position of the edge of the ultra-violet absorption was the same for both concentrations. The absorption bands were found to be more intense for the dilute solution. Uranyl chloride in concentrations $c_1 : c_2 = 2500 : 1$

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[1] *Loc. cit.*

showed three absorption bands, *a* (λ 4950–4870), *b* (λ 4820–4720), and *c* (λ 4650–4560). The bands were unaffected by dilution.

Knoblauch considers that deviations from Beer's law must be due to (1) a change in the molecular complex that constitutes the absorber; (2) a chemical change such as hydrolysis or hydration; (3) dissociation; (4) mutual actions which exist between the dissolved molecules in concentrated solutions that do not occur in very dilute solutions. The experimental results which he obtains for uranyl and eosin salts indicate that deviations from Beer's law can not be explained as being due to dissociation.

Hartley has made an interesting observation on uranyl nitrate, $UO_2(NO_3)_2.6H_2O$. He finds on dissolving this crystalline nitrate in ether that the water of crystallization does not act as ordinary water and mix with the ether, but that it remains in combination with the uranyl nitrate. It would be interesting to find the effect of change in temperature on this water. In this connection it is very important to determine the transference numbers for the various uranyl, uranous, and neodymium salts in different solvents and mixtures of these solvents. The amount of heat absorbed or given off when salts containing a different number of molecules of the solvent of crystallization are dissolved should also be determined. These data are necessary in order that the facts obtained by spectrum analysis may be properly interpreted. In the case of uranium or neodymium it is probable that only a few of the atoms are concerned with the absorption, and the condition of the great mass of the atoms may differ very greatly from that of the few that are taking part in the absorption of light.

Deussen[1] has made a very complete examination of the absorption spectra of various uranyl salts in different solvents and in mixtures of different solvents. Below are the wave-lengths measured by Deussen:

URANYL NITRATE.

Solvent.	*a.*	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*	*j.*
Water	4860	4720	4540	4380	4290	4150	4020	3870	3790	3690
Ethyl alcohol	4845	4680	4490	4360	4240	4090	3990	3840	3750	3660
Methyl alcohol	4850	4680	4490	4360	4295	4050	4000	3840	3750	3660
Acetone	4845	4680	4490	4360	4240	4090	3990	3855	3760	3670
Glycerol	4870	4735	4525	4350	4220	4060	3910	3820	3710	....
Amyl alcohol	4845	4680	4490	4360	4240	4090	3990	3840	3750	3660
Acetic ester	4850	4685	4495	4365	4250	4095	3995	3845	3755	3665
Ether	4850	4685	4495	4370	4255	4100	4000	3850	3760	3670

The above wave-lengths of the bands do not agree very well with our own measurements. For instance, the ethyl alcohol-bands are found to have a greater wave-length than the water-bands. Deussen worked with mixtures of all the above solvents and water. He obtained some very remarkable results. For example, he finds that, as compared with a pure aqueous solution of uranyl nitrate, in the 50 per cent ethyl alcohol solution all the uranyl bands are shifted towards the red. When the solvent con-

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[1] *Loc. cit.*

tains 80 per cent alcohol all the bands are shifted towards the violet, and for a pure alcohol solution all the uranyl bands are of shorter wave-length than for a pure aqueous solution.

Deussen obtained very interesting results for uranyl nitrate in mixtures of water and glycerol. As the percentage of glycerol increases the *c* and *d* bands broaden and finally, for a pure glycerol solution, form but a single band. At the same time all the other bands are shifted towards the red.

URANYL CHLORIDE.

Solvent.	*a.*	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*	*j.*	
Water	4900	4735	4580	4410	4285	4140	4025	3925	3800	3710	....
Ethyl alcohol ...	4910	4745	4595	4425	4305	4200	4080	3990	3870	3750	....
Glycerol	4920	4755	4600	4510	4410	4280	4170	4030	3940	3810	3715

For uranyl chloride solutions in mixtures of water and glycerol, Deussen finds that the *c* band of the aqueous solution breaks into two bands when the solvent is pure glycerol. Increasing percentages of glycerol cause an increased shift of the bands towards the red.

URANYL SULPHATE $(UO_2SO_4.3H_2O)$.

Solvent.	*a.*	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Water...........	4885	4725	4560	4410	4310	4180	4060	3950
Ethyl alcohol.....	4890	4730	4565	4420	4320	4190	4070	3960
Glycerol..........	4890	4730	4570	4430	4340	4210	4090	3980

H. Becquerel[1] has made a number of observations on the absorption spectra of uranium compounds at low temperatures. He considers that the absorption and phosphorescent bands are parts of a single system. They have two bands in common. He states that any modification in the appearance of one set of bands for any compound is reproduced by a similar change in the other set of bands. In general, the bands found at the temperature of liquid air are moved towards the violet with respect to the same bands at ordinary temperatures. Uranyl nitrate, at ordinary temperatures, gives wide diffuse bands whose intensities are at a maximum at their middle. At the temperature of liquid air each group is resolved into several centers, and the most intense of these bands are towards the violet. A table of the wave-lengths of these bands is given below.

Bois and Elias[2] find that the double sulphate of uranyl and potassium when cooled to – 190° gives bands at λλ 4878, 4882, 4888, and 4905. These seem to broaden slightly when placed in a strong magnetic field. At 18° uranyl nitrate gives bands at λ 4675–4716, λ 4849–4880, and at – 190° C. strong bands at λ 4679–4697, λ 4845–4849, and λ 4853–4857.

Uranous salts are of a deep green color and have a very characteristic absorption spectrum, which consists of diffuse bands scattered throughout

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[1] Compt. rend., **101**, 1252 (1885); **144**, 459, 671 (1907).

[2] Ann. Phys., **27**, 299 (1908).

the spectrum. With the exception of a short description of a few of the bands by Formánek, practically nothing has been done on the absorption of uranous salts either in solution or in the crystalline condition.

Crystals of uranyl nitrate.		Double sulphate of uranyl and potassium.		Double chloride of uranyl and potassium.	
Room temperature.	Liquid air.	Room temperature.	Liquid air.	Room temperature.	Liquid air.
Diffuse band.			6500	6400–6360	
	6360		6270	6315	6360
	6170(s)		6185–6175		
6201–6150	6145–6127	6155 weak	6155–6145(s)		
	6104		6039–5945	6055	6030(s)
	6050				5800
			5910(f)	5970–5975	5751(s)
	5856(s)	5890–5885	5887(s)	5920	
	5833(s)		5830	5776–5740(s)	5721(f)
	5782		5763	5702(f)	
	5707	5760	5715	5632(t)	5619(f)
	5630		5695–5674	5515–5481(s)	5555(f)
	5600		5647(s)	5447	5535
	5580(s)	5610–5560	5616(s)	5394(f)	5486(s)
	5553(s)		5591(s)	5275–5247(s)	5462(f)
	5490	5535	5886	5205	5435(t)
	5435	5515	5410	5161(f)	5400(f)
	5375		5427(t)	5116(f)	5373(f)
	5323(s)		5384(f)	5080(t)	5361(f)
	5297(s)		5365(s)	5065(t)	5315(f)
	5272		5347	5042	5295(s)
	5240		5338(s)	4995	5224(s)
	5190		5334		5202(f)
	5137		5138		5156(f)
5120–5060	5115		5124(f)		5196(f)
	5093(s)		5114(s)		5072
	5072(s)		5000		5040(s)
	5018		4932(s)		5012
4893–4855	4975		4910(s)		4990(f)
	4925				
	4900(s)				

THE ABSORPTION SPECTRUM OF URANYL CHLORIDE.

The absorption spectrum of uranyl chloride (crystals having the composition $UO_2Cl_2.H_2O$ at ordinary temperatures) has been mapped for solutions in water, methyl and ethyl alcohols, in mixtures of these solvents and in solutions with aluminium and calcium chlorides and for the anhydrous salt.

Uranyl Chloride in Aqueous Solutions.

The absorption spectrum (Plate 48, *B*) of uranyl chloride in water was mapped for 1, 0.75, 0.50, 0.33, 0.25, 0.16, and 0.125 normal solutions, the depth of layer being 3 mm. and the time of exposure to the Nernst glower with a current of 0.8 ampere being 1 minute. The slit-width was 0.08 mm.

The absorption spectra of the chloride and bromide are very similar, the blue-violet absorption band being slightly stronger for the chloride. The uranyl bands are very broad and diffuse for both salts, being slightly more diffuse for the chloride. Practically only the *a*, *b*, and *c* bands appear with any strength.

Of these, *a* and *b* are the stronger. They appear of about the same intensity and are about 80 Ångström units wide. For the bromide *a* is considerably weaker than *b*. The sulphate and nitrate, on the other hand, show practically all of the uranyl bands, the bands being the strongest in the sulphate solution. In this salt solution the *b* and *c* bands are six to ten times as strong as the *a* band. In the nitrate this difference is not so marked, and the bands appear somewhat finer than in the case of any other salt. The acetate shows the greatest absorption of the salts mentioned above. Here, the *a*, *b*, and *c* bands are very faint. About half a dozen very faint bands appear together.

For the normal solution the ultra-violet and blue-violet bands merge together and end at λ 4550. For the 0.75 normal solution the blue-violet band is limited by regions of absorption beyond the limits $\lambda\lambda$ 4500 and 3900, for the 0.5 normal solution, $\lambda\lambda$ 4470 and 3950, and for the 0.33 normal solution, $\lambda\lambda$ 4400 and 4050, the center of the band thus being at λ 4200. Collecting the results of their measurements of the center of this blue-violet band we have:

Uranyl chloride	λ 4200
Uranyl nitrate	λ 4150
Uranyl bromide	λ 4250
Uranyl acetate	λ 4200
Uranyl sulphate	λ 4180

Therefore, for all these salts the blue-violet bands appear at the same position.

The band also widens with increase in concentration quite uniformly. The edges of the ultra-violet band are: 0.75 normal λ 3700, 0.5 normal λ 3670, 0.33 normal λ 3650, 0.25 normal λ 3630, 0.16 normal λ 3600, and 0.125 normal λ 3570.

The positions of three of the uranyl bands (*a*, *b*, and *c*) were measured. On account of the extreme faintness of *c* the result for this band is not very accurate: *a*, 4920; *b*, 4740; *c*, 4560; *d*, 4460; *e*, 4315; *f*, 4170; *g*, 4025.

In addition to the bands already given, uranyl chloride has several remarkably fine bands in the green. These bands are not more than 5 Ångström units wide and were first seen on spectrograms made on the Wratten and Wainwright red-sensitive films. They appear only for aqueous solutions of uranyl chloride. The addition of calcium or aluminium chloride causes them to disappear. They do not appear in the alcoholic solutions. Uranyl sulphate shows the same bands at about the same position as the chloride but much weaker—too weak to be separated. The wave-lengths are as follows: $\lambda\lambda$ 5185, 5200, 6000, 6020, 6040, and 6070.

So far as the writers know, this is the first time that these bands have been noticed in aqueous solutions. Uranyl salts give a spectrum of emission through phosphorescence, and this spectrum appears to be a continuation of the absorption spectra to longer wave-lengths. Becquerel[1] has

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[1] Mém Acad. Sci., 40 (1872).

found that any uranyl compound showing a modification of the absorption bands shows a similar modification of the emission phosphorescent bands.

A series of spectrograms was made to test Beer's law. Exposures were made under the standard conditions with 1, 0.75, 0.5, 0.33, 0.25, 0.16, and 0.125 normal solutions of uranyl chloride, the corresponding depths of cell being 3, 4, 6, 9, 13, 18, and 24 mm.

There is a slight transmission band in the ultra-violet between the blue-violet and ultra-violet bands. This transmission region is roughly 100 Ångström units wide, and is so faint that it does not appear upon the printed plates. This band obeys Beer's law. The long wave-length edge of the blue-violet absorption band, however, deviates slightly from Beer's law. For the 1, 0.75, 0.5, and 0.33 normal solutions the absorption is slightly greater than for the 0.25 normal solution. The 0.25, 0.16, and 0.125 normal solutions obey Beer's law. The edge for the 1 normal solution is roughly 75 Ångström units nearer the red than for the 0.25 normal solution. The uranyl bands *a* and *b* are slightly stronger for the more concentrated solutions. A similar run for Beer's law was made between the concentrations 0.125 and 0.0156 normal. Beer's law holds in this case, the absorption being complete for wave-lengths less than λ 4150. The uranyl bands do not appear at all.

URANYL, CALCIUM, ALUMINIUM, AND ZINC CHLORIDES IN WATER; URANYL CHLORIDE AND HYDROCHLORIC ACID IN WATER.

Plate 52, *A* and *B*. were taken for aqueous solutions of uranyl chloride of a constant concentration to which varying amounts of calcium chloride were added. The addition of calcium chloride causes the ultra-violet, the blue-violet, and the uranyl bands to widen generally. The effect upon the uranyl bands is, however, very small. The effect of aluminium chloride, shown in Plate 51, *A* and *B*, on the other hand, is very great. The two narrow and faint bands at λ 5200 appear only in the pure aqueous solution of uranyl chloride. The *a* band in the aqueous solution is about 60 Ångström units wide, and is almost as intense as the *b* band. The addition of aluminium chloride causes the band to become quite narrow, about 25 Ångström units wide. A slight addition of aluminium chloride decreases the intensity of the band very considerably. Further increases in the amount of aluminium have very little effect. The addition of aluminium chloride also causes the bands to shift to the red, the shifts in some instances amounting to 25 Ångström units. The intensity of the *b* and *c* bands is very greatly increased by the addition of aluminium chloride; and by making the solution about 2 normal with aluminium chloride these bands are shifted about 30 Ångström units to the red as compared with the same bands for the pure uranyl chloride solution. The *d*, *e*, *f*, *g*, and *h* bands are also increased in intensity, but are only very slightly shifted to the red. The *d* and *e* bands are widened so that they form practically a single band.

In order to bring out the similarity of the action of aluminium chloride on uranyl and on uranous chlorides, the absorption spectra of a 0.2 normal solution of uranyl chloride in water (Plate 49, *A*), and of a 0.2 normal solution of uranyl chloride and a 2.4 normal solution of aluminium (Plate 49, *B*) were made. The depths of layer were 3, 6, 12, 24, and 35 mm. In our discussion of the uranyl salts the effect of aluminium chloride was described. The different effect of the aluminium chloride upon the *a* and *b* bands is very marked. In the uranous solution the *a* band does not appear, and in fact the bands here do not seem to coincide very well either in position or intensity with the bands of uranyl chloride in water. The position of the uranyl bands when aluminium chloride is added is: *a*, 4950; *b*, 4790; *c*, 4620; *d*, *e*, 4480–4420; *f*, 4270; *g*, 4135; *h*, 4010.

(1) In uranyl chloride in aqueous solutions the addition of aluminium chloride makes the uranyl bands much stronger. It causes the *d* and *e* bands to come together to form practically one band.

(2) In aqueous solutions of uranous chloride the addition of aluminium chloride before the uranyl salt was produced causes the uranyl bands to appear, the position of these bands being the same as in case 1.

(3) The presence of aluminium chloride in both cases causes a greater ultra-violet absorption.

The effect of hydrochloric acid and zinc chloride on the uranyl bands is very similar to that of aluminium chloride.

Solutions of 0.2 normal concentration were made in very strong hydrochloric acid and zinc chloride solutions. These are represented by Plate 50, *A* and *B*. The four spectrograms (Plates 49 and 50, *A* and *B*), were all made under the same condition. Zinc chloride, hydrochloric acid, and aluminium chloride have the common property of making the uranyl bands much stronger. Hydrochloric acid and aluminium chloride increase the ultra-violet absorption and cause the uranyl bands to shift much more towards the red than zinc chloride does. The following table gives the wave-lengths of the uranyl bands in aqueous solutions when the above named substances are added:

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
Pure UO_2Cl_2	4920	4740	4560	4460	4315	4170	4025	....	....
+ $ZnCl_2$	4930	4770	4600	4400 very wide	....	4245	4115	....	....
+ $AlCl_3$	4950	4790	4620	4480	4420	4270	4135	4010	....
+ HCl	4950	4800	4635	4480	4420	4280	4150	4015	....

The bands of the aluminium chloride and hydrochloric acid solutions do not coincide, and the relative displacements show very clearly when the two original films are placed together so that the spark lines coincide. In none of these spectrograms do the "characteristic" uranyl chloride bands appear, probably on account of the large slit-width.

The zinc chloride solution was made by dipping zinc in hydrochloric acid of the same strength as was used to make the UO_2Cl_2 solution in hydrochloric acid. To the zinc chloride and hydrochloric acid solutions a normal solution of uranyl chloride was added so as to make the resulting uranyl chloride solution 0.2 normal.

Uranyl Chloride in Methyl Alcohol.

The first spectrogram for mapping out the absorption spectrum of uranyl chloride in methyl alcohol is given in Plate 53, *B*. Exposures were made to the Nernst glower for 1 minute with a slit-width of 0.08 mm. and a current of 0.8 ampere. The depth of cell is 6 mm. for each strip. Beginning with the strip nearest the numbered scale, the concentrations are 0.0625, 0.079, 0.1, 0.125, 0.158, 0.2, and 0.25 normal.

The alcoholic solution of uranyl chloride is very similar to the alcoholic solution of uranyl nitrate, the absorbing power of both solutions being considerably greater than that of aqueous solutions. The aqueous solution of uranyl chloride shows only a few of the characteristic uranyl bands in its absorption spectrum. In the alcoholic solution, however, they appear very strongly.

Starting with the most concentrated solution, whose absorption spectrum is given by the strip furthest from the numbered scale, we have the bands *a* and *b* appearing and all wave-lengths less than λ 4500 completely absorbed. The *b* band is very strong, the *a* band very weak—almost lost in this region of the spectrum where the film is less sensitive to the light. For the next concentration, 2 normal, we have a weak transmission band appearing in the ultra-violet. Other uranyl bands appear as the concentration is decreased. We shall now consider the blue-violet band. For the 0.2 normal solution its limits are λλ 4450 and 3800, for the 0.158 normal solution λλ 4400 and 3900, and for the 0.125 normal solution λλ 4350 and 3900. The middle of the band would thus come at about λ 4100.

The uranyl bands *a, b, c, d, e, f, g, h, i,* and *j* all appear. The bands *b* and *c* are the largest and strongest. Band *a* is relatively much weaker. The appearance of the bands is somewhat like the bands of uranyl nitrate in methyl alcohol. The uranyl nitrate bands are, on the whole, considerably fainter and narrower than the uranyl chloride bands. Bands *a, b,* and *c* are almost of the same intensity in the case of the nitrate, all being quite faint. The blue-violet band is much more diffuse in the spectrum of the uranyl nitrate. The following are the wave-lengths of the bands of uranyl chloride, the second row giving the wave-lengths of the same bands for uranyl nitrate in methyl alcohol:

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*	*j.*
Chloride.........	4930	4760	4610	4465	4345	4220	4090	3980	3860	3760
Nitrate..........	4930	4760	4610	4460	4325	4190	4070	3970	3855	....

The *a, b,* and *c* bands of the chloride and nitrate come at about the same positions, but the *e, f, g,* and *h* bands of the chloride are all shifted towards the red as compared with the same bands of the nitrate. The uranyl chloride bands in water are slightly shifted towards the violet with reference to the uranyl chloride bands in methyl alcohol.

The relative intensities of the bands do not completely agree with those given by Deussen.[1] In the main, the results agree fairly well with his; he finding that in alcohol the bands are shifted towards the red.

Plate 55, *A*, was made in exactly the same way as Plate 53, *B*, the only difference being that the depth of cell was 15 mm. whereas for the spectrogram previously described the depth of cell was only 3 mm. This spectrogram shows very well how a uranyl band increases in intensity as the edge of the blue-violet band approaches it.

The *a* band thus increases in intensity and in width with increase in concentration. The band also seems to widen unsymmetrically, although the disymmetry may be due in part to the unequal sensitiveness of the photographic film to different wave-lengths of light in this part of the spectrum.

The spectrogram Plate 53, *A*, taken to test Beer's law, was made by exposures of 1 minute to the Nernst glower with a current of 0.8 ampere, and slit-width of 0.08 mm. Exposures to the spark in order to get reference lines were made only in the ultra-violet. Starting with the strip next to the numbered scale, the concentrations were 0.0625, 0.079, 0.1, 0.125, 0.158, 0.2, and 0.25 normal, the corresponding depths of cell being 24, 19, 15, 12, 9.5, 7.5, and 6 mm.

Beer's law holds for the alcoholic solutions between 0.25 normal and 0.06 normal. The limit of absorption is at λ 4650 and is quite sharp, this being the long wave-length edge of the uranyl *c* band. The *b* band is very strong, the *a* band quite weak.

A very faint transmission band appears at λ 3850 and is about 100 Ångström units wide. This band also obeys Beer's law and is, in fact, quite a sensitive index for any deviations from this law.

Uranyl Chloride and Calcium Chloride in Methyl Alcohol.

Plate 54, *A and B.*—These spectrograms, showing the absorption spectra of mixtures of uranyl chloride and calcium chloride in methyl alcohol, were taken under the same conditions. Exposure was made to the Nernst glower for 1 minute with a slit-width of 0.08 mm. and a current of 0.8 ampere. The ultra-violet standard lines were photographed with the uranyl solution removed from the light beam. In every case the concentration of uranyl chloride was 0.125 normal. Starting with the strip at the top of the spectrogram of both *A* and *B* the concentrations of calcium chloride were 0.0, 0.144, 0.0288, 0.432, 0.576, 0.72, and 0.9 normal. In *A* the depth of solution was 6 mm., in *B* 3 mm.

The effect of calcium chloride on the absorption spectra of a methyl alcohol solution of uranyl chloride is very slight, notwithstanding the power of calcium chloride to combine with alcohol. An increased amount of calcium chloride causes the ultra-violet and blue-violet bands to widen slightly, as will be seen from both *A* and *B*. The change in the intensity of the uranyl bands is also very slight.

In the upper strip of *B* appear the bands *a*, *b*, *c*, *d*, *e*, *f*, *i*, and *j*. Only one edge of *a* is to be seen clearly; *b* and *c* are clear and entirely separated;

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[1] Ann. Phys., 66, 1137 (1898).

d is very diffuse and especially so on the violet side; *e* is also diffuse but is a distinct band. *f*, *g*, and *h* are distinct and entirely separated; *i* and *j* can also be noticed. When calcium chloride is added a very peculiar phenomenon manifests itself. The bands *d* and *e* come together and, as far as one can tell, form a single band. This causes the bands *f*, *g*, and *h* to shift to the red, the other bands becoming too faint to be recognized. Measurements gave the following wave-lengths for the solution of uranyl chloride in methyl alcohol itself: *b*, λ 4760; *c*, λ 4590; *d*, λ 4465; *e*, λ 4345; *f*, λ 4225; *g*, λ 4095; *h*, λ 3975; and *i*, λ 3860. Taking up the solution containing a 0.9 normal concentration of calcium chloride we find that the *b* and *c* bands have remained at the same part of the spectrum. The *d* and *e* bands have combined into one large, diffuse band whose position is approximately λ 4420. The *f*, *g*, and *h* bands are now at $\lambda\lambda$ 4260, 4120, and 4010, respectively.

A spectrogram was also taken under conditions identical in every respect with those in *A* and *B*, except that the depth of layer was made 15 mm. Here only the *a* and *b* bands appeared. The *b* band was very wide and strong, the *a* band very weak. In the pure uranyl chloride solution the *a* band was quite wide. As the amount of calcium chloride was increased the band became much narrower, and its center shifted from λ4925 for the pure uranyl chloride solution to about λ 4895 for the solution containing a 0.9 normal concentration of calcium chloride. Whether this could be accounted for as due entirely to unsymmetrical narrowing is uncertain, though it seemed that its short wave-length edge was slightly shifted towards the violet.

URANYL CHLORIDE IN METHYL ALCOHOL AND WATER.

Since the uranyl chloride bands are different in position in water from what they are in methyl alcohol, several spectrograms were made of mixtures of alcohol and water. *A* and *B*, Plate 56, are two examples. The exposures were 1 minute to the Nernst glower, slit-width 0.01 mm. and current 0.8 ampere. An exposure of 1 minute to the spark was also made in the ultra-violet with the solution taken out of the path of the beam of light. The top strip of both *A* and *B* represents a 0.1 normal solution of uranyl chloride in methyl alcohol. In the remaining cases the concentration of uranyl chloride is kept the same and the depth of cell the same. The solvent, however, contains more and more water. The second strip was made using a solution containing 50 per cent water, the third 40 per cent, the fourth 32 per cent, the fifth 24 per cent, the sixth 16 per cent, and the seventh 8 per cent water. For *A* the depth of cell was 16.7 mm., for *B* 6 mm.

It will be seen that a small addition of water causes a considerable decrease in the absorptive power of the uranyl chloride. The decrease of absorbing power is much less after the amount of water has reached 16 per cent. The pure alcohol solution in *A* does not show any transmission in the ultra-violet at all. The 8 per cent aqueous solution shows a slight transmission, the 16 per cent aqueous solution a somewhat stronger transmission. Increase of water beyond this amount increases the intensity of this band very slightly.

The most important effect of the addition of water is the *reducing of the intensity and changing the position of the uranyl chloride bands.* In *A*, the bands *a* and *b* appear in the pure alcoholic solution. The *b* band is very intense. As the amount of water is increased *a* disappears, only one edge of it being recognizable in a 16 per cent aqueous solution. *b* is greatly reduced in intensity and is shifted towards the violet by the addition of water. *B* shows still better this effect upon the uranyl bands. In the alcoholic solution the bands *a*, *b*, *c*, *f*, *g*, *h*, and *i* appear. In the 8 per cent aqueous solution *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i*, *j*; in the 16 per cent aqueous solution *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i*, and *j*; in the 24 per cent aqueous solution the bands are much weaker and in the strips showing a greater amount of water than this, practically only *b* and *c* are visible—and these two bands are extremely faint. The greatest effect appears before the amount of water is greater than 20 per cent. The general effect upon the position of the uranyl bands is quite remarkable—the *b* and *c* bands are shifted towards the violet with increase of water, whereas the ultra-violet bands appear to be shifted towards the red.

Uranyl chloride in—	*a.*	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*		
Water	4920	4740	4560	4460	4315	4170	4025		
CH_4O	4930	4760	4590	4465	4345	4220	4090		
$CaCl_2$ } CH_4O }	4930	4760	4590	4420		4260	4120	4010	
C_2H_6O	4900	4750	4580	4400		4250	4100	3980	3860
Water and $AlCl_3$	4950	4790	4620	4480–4420		4270	4135	4010	

Uranyl Chloride in Ethyl Alcohol.

Plate 58, *B*, represents the absorption spectra of an ethyl alcohol solution of uranyl chloride, the depth of cell being kept constant 6 mm. and the concentration varied. Starting with the upper strip the concentrations were 0.25, 0.2, 0.158, 0.125, 0.1, 0.079, and 0.0625 normal. The strips were each exposed 1 minute to the Nernst glower, slit-width being 0.08 mm., current 0.8 ampere. A comparison spectrum was also taken, exposure being in this case 1 minute, the solution having previously been removed from the source of light.

The spectrogram shows the blue-violet band whose center is about λ 4250 and also the ultra-violet band. The blue-violet band gradually disappears when the concentration is less than about 0.10 normal. The uranyl bands come out quite strongly, but are not as intense as in the methyl alcohol solution. The bands in ethyl alcohol occupy the same positions as the uranyl bands do in a solution in methyl alcohol in which there is 0.9 normal concentration of calcium chloride. In the 0.25 normal solution the *a* band has divided into two faint bands whose centers are about λ 5000 and λ 4900; the *b* band is at λ 4750, *c* at λ 4585, *d* and *e* at λ 4400, *f* at λ 4250, *g* at λ 4100, *h* at λ 3985, and *i* at λ 3865.

The character of the *a* band is shown in *A*, Plate 57. This spectrogram was taken under the same conditions as *A*, Plate 58, except that here the depth of cell was 15 mm., whereas in the other spectrogram it was 6 mm.

A, Plate 58, is a spectrogram to test Beer's law, the length of exposures and concentrations being the same as for *B*. Instead of the depth of cell being constant, this was changed so that the product of depth of cell and concentration remained constant. Beer's law was found to hold. In this spectrogram the *a* band is shown to be broken up into two other bands. The *a* and *b* bands also obey Beer's law. In the ultra-violet there is a faint transmission band. This also is unaffected by change in concentration.

Uranyl Chloride in Glycerol.

A and *B*, Plate 59, represent the absorption spectra of a solution of uranyl chloride in glycerol, the depth of cell being 10 and 5 mm., respectively. The concentrations, starting with the strip nearest the scale, were 0.176, 0.132, 0.088, 0.059, 0.041, 0.032, and 0.022 normal. The spectrograms are very similar to those of the other uranyl salts. The blue-violet absorption band vanishes at about λ 4300. The positions of the uranyl bands are: *a*, 5050; *c*, 4720; *d*, 4540; *e*, 4400; *f*, 4260; *g*, 4140; *h*, 4025; and 3920.

The uranyl bands of a glycerol solution are quite broad. The same is true of the uranous bands. Glycerol usually has the effect of making the bands less dense than they appear for most of the other solvents. In a few cases the bands are quite fine, however, as in the case of the erbium and neodymium salts.

Uranyl Chloride in Mixtures of Glycerol and Methyl Alcohol.

Spectrograms *A* and *B* (Plate 60) represent the absorption of a solution of uranyl chloride in mixtures of glycerol and methyl alcohol. The depth of cell for *A* was 25 mm., *B* 3 mm. The concentration of uranyl chloride was 0.0176 normal. The percentages of methyl alcohol were 0, 15, 30, 45, 60, 75, and 90.

The general ultra-violet absorption remains about the same for the various mixtures of the solvents. The uranyl bands change but slightly, the *b*, *c*, and *d* bands being the only ones that change. The *b* band of the upper strip has a weak component at λ 4800, the *c* band at λ 4660, and the *d* band appears double. The wave-lengths of the bands remain practically the same as for the pure glycerol solution. The methyl alcohol bands, however, are quite different in position from the glycerol bands, and from these spectrograms we see that practically all the change must occur between a 90 per cent and a 100 per cent methyl alcohol mixture; the glycerol bands being much more persistent than the alcohol bands.

Uranyl Chloride in Acetone and the Effect of Hydrochloric Acid on the Uranyl Acetate Bands.

A solution of uranyl chloride (3 grams in 100 c.c. acetone) was made and the absorption spectra of depths of layer of 3, 6, and 15 mm. were taken. Depths of 1.5, 3, and 9 mm. were then used of the above acetone solution, to which an equal volume of strong hydrochloric acid had been added. The addition of hydrochloric acid causes the solution to become very red. Upon the spectrogram there were 7 strips. The addition of hydrochloric acid caused the uranyl bands to break up into several components. It also caused a very great amount of increased absorption throughout the spectrum. Strip 1 showed absorption of the shorter wave-lengths to λ 3800, strip 3 to λ 4700, strip 4 to λ 3700, strip 5 to λ 4200 (and a broad diffuse band at λ 5100), strip 6 to λ 6000, and strip 7 to λ 6300, approximately. For the solution containing hydrochloric acid the uranyl bands are not as strong as for the pure acetone solution. The wave-lengths of the uranyl bands are as follows (in acetone):

a 4960 to 4930
b 4795 to 4760
c 4645*n*, 4630, 4600
d 4470*b*
e 4320*b*
f 4180
g 4040

In the pure acetone solution the *a*, *b*, and *c* bands each contain two bands of about equal intensity, that almost blend into a single band. There are fine bands at λλ 4980, 5000, 5030, 5240, 5270, and 5295.

URANYL CHLORIDE IN ACETONE AND WATER.

A spectrogram was made showing the way the uranyl bands of an acetone solution are affected by hydrochloric acid and water. Strip 1 is the absorption of a 2 mm. solution of 0.0088 normal uranyl chloride in acetone; strip 2 is the same to which hydrochloric acid has been added so as to make a depth of cell of 3.2 mm.; strip 3, where water has been added to make a depth of cell of 3.4 mm.; strip 4 to 4 mm.; strip 5 to 5 mm.; and strip 6 to 11 mm. In the latter case a white precipitate was formed.

The addition of hydrochloric acid causes the uranyl bands to break into various components. The addition of water causes these components to broaden, weaken, and finally to form very faint, diffuse bands. As long as the components appear their wave-lengths remain unchanged as water is added.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
Strip 2	4930(20)	4765(30)	4605(30) 4550(*f*30)	4470(*w*20) 4430(*s*20) 4385(*w*20)	4340(*w*20) 4290(*s*20) 4250(*w*20)	4205(*w*20) 4160(*s*20) 4120(*w*20)	....
Strip 5	....	4770(*f*)	4610(*f*)	4430(*f*)	4250(*f*)	4130(*f*)	

URANYL CHLORIDE, TEMPERATURE EFFECT.

A spectrogram (Plate 61, *A*) was made of the absorption spectrum of a normal aqueous solution of uranyl chloride, the depth of cell being 3 mm. Exposures were made to the Nernst glower for 90 seconds (current 0.8 ampere and slit-width 0.20 mm.). The time of exposure to the spark was 6 minutes. Starting from the comparison spectrum, the temperatures were 6°, 18°, 34°, 52°, 68°, and 82°.

At 8° the ultra-violet band extended to λ 3550, the blue-violet band from λ 4000 to λ 4450. The bands *a*, *b*, and *c* appeared, but the *a* band is very faint. The wave-lengths of the *b* and *c* bands were λλ 4565 and 4725.

At 82° the ultra-violet band extends to λ 3700, and the blue-violet band from λ 3950 to λ 4600. At this temperature only the *b* band appears, *a* being very weak and *c* completely merged into the blue-violet absorption band. The *b* band is located at λ 4755.

A spectrogram (Plate 61, *B*) was made of a 0.0156 normal aqueous solution of uranyl chloride 196 mm. deep. Exposures were made to the Nernst glower for 30 seconds (current 0.8 ampere and slit-width 0.20 mm.). No exposures were made to the spark except for comparison spectra. Starting with the numbered scale, the temperatures were 6°, 18°, 29°, 44°, 59°, 71°, and 79°.

For this concentration there is a very slight temperature effect. There is a very faint transmission band between the ultra-violet and blue-violet bands. This is extremely faint and is practically unaffected by temperature. The blue-violet band widened slightly with rise in temperature. The uranyl bands in the concentrated solution were much stronger and wider than in the dilute solution.

Absorption Spectrum of Anhydrous Uranyl Chloride.

The absorption spectrum of the anhydrous chloride was photographed in the same way as that of the anhydrous nitrate. The bands differ considerably from the bands of the aqueous solution, and one cannot tell very well whether they are identical with the corresponding *a*, *b*, *c*, etc., bands of the solution or not. Their wave-lengths are approximately as follows: λλ 4950 (narrow), 4860, 4765, 4700, 4615, 4540, 4460, 4320, 4290, 4160, 4050, and 3940.

ABSORPTION SPECTRUM OF URANYL NITRATE UNDER DIFFERENT CONDITIONS.

Uranyl Nitrate in Aqueous Solution.

The spectrum of uranyl nitrate in water is a typical example of the uranyl salts. With a depth of solution of 3 mm. its absorption spectrum (Plate 62, *A*, *B*) was investigated between concentrations of 1.5 normal and 0.0234 normal. For the 1.5 normal solution the absorption consists of a band in the blue-violet and absorption throughout the ultra-violet portion of the spectrum. As the concentration decreases the blue-violet band fills up with transmission, and the ultra-violet absorption is pushed farther and farther out into the ultra-violet. The blue-violet band is practically gone at a concentration of 0.5 normal, and there is almost complete transmission throughout the ultra-violet for concentrations less than 0.02 normal.

During these changes in concentration a large number of bands about 50 Ångström units wide make their appearance. Near the edge of an absorption band these bands are relatively quite clear. As the absorption edge recedes from the uranyl bands, the general transmission is so great as to obscure them almost completely.

A, Plate 63, represents the absorption spectra of an aqueous solution of uranyl nitrate of different depths of layer. The narrow and rather weak bands shown here are the uranyl bands. Twelve of these bands have been photographed. Starting with the band of longest wave-length they will be designated by the letters *a*, *b*, *c*, *d*, etc. On account of the irregularity of the distribution of light in the spark-spectrum and the small intensity of the uranyl bands, the Nernst glower was used as the source of light in the ultra-violet, and long exposures were made. A screen was used that cut out all wave-lengths greater than λ 4200. *A* represents a typical spectrogram of this kind. Starting with the spectrum-strip at the top, the concentrations were 1.5, 1.1255, 0.75, 0.5, 0.375, 0.25, and 0.1875 normal. The slit-width was 0.08 mm. and the current through the Nernst glower 0.8 ampere. The spectra of wave-lengths greater than λ 4300 represent the absorption of a depth of layer of 15 mm.; the spectra of shorter wave-lengths represent the absorption of a depth of layer of 3 mm. The upper spectrum-strip represents, then, the absorption spectrum of a 1.5 normal solution of uranyl chloride 15 mm. thick, exposure to the Nernst glower having been 1 minute. It will be seen that the uranyl band *a* comes out very strongly. The screen was then placed in the path of light and exposure of 5 minutes made to the violet and ultra-violet beyond λ 4300; a solution of uranyl nitrate of 1.5 normal concentration and 3 mm. deep being in the path of the beam of light. This amount of uranyl nitrate absorbed practically all the light in this region. A very short exposure was afterwards made to the spark in the region λ 2600, in order to get a comparison spark-spectrum in this region, so that the wave-lengths of the uranyl bands could be measured.

Throughout this work a comparison spark-spectrum usually containing the very strong line λ 2478.8 was photographed on each spectrum-strip. In measuring the uranyl bands all measurements were made from this line as a standard, and although the absolute wave-lengths of the uranyl bands may not be correct to within 20 Ångström units, yet relatively they are probably correct to within less than 10 Ångström units for the finer bands.

The second spectrum-strip from the top represents in the long wave-length end of the spectrum, the absorption of a 15 mm. layer of a 1.125 normal solution of uranyl nitrate exposed 1 minute to the Nernst glower. The *a* band appears, although not nearly as intense as in the spectrum-strip above. The region of shorter wave-lengths beyond λ 4300 represents the absorption of a 3 mm. layer of a 1.125 normal solution exposed 5 minutes to the Nernst glower. A very faint transmission is shown in the region λ 3700. The ultra-violet line λ 2478.8 is shown in the comparison spark-spectrum. The other spectrum-strips were made in a similar manner, with the concentrations given above.

By this method of exposing, two new bands were detected in the ultra-violet. In aqueous solutions the intensities of the bands are much the same. In other solvents, however, and for other uranyl salts, the relative intensities of the bands change very greatly. For uranyl nitrate crystals the bands are even more closely related to each other than in aqueous solutions. The longer the wave-length of the band the more intense and wider it is as a rule. The position of the long wave-length bands in the orthorhombic uranyl nitrate crystals, $UO_2(NO_3)_2 6H_2O$, is the same as the position of the bands for an aqueous solution. The wave-lengths of the bands are as follows:

Band.	Aqueous solution.		Crystals.	Band.	Aqueous solution.		Crystals.
	Deussen.	Jones and Strong.			Deussen.	Jones and Strong.	
a	4860	4870	4870	*g*	4020	4030	4050
b	4720	4705	4705	*h*	3870	3905	3935
c	4540	4550	4500–4565	*i*	3790	3815	3830
d	4380	4390	4405	*j*	3690	3710	(3720?)
e	4290	....	4275	*k*	....	3605	3600
f	4150	4155	4170	*l*	....	3515	....

In the original film from which *A*, Plate 63, was made all of these bands except *d* could be very distinctly seen. The bands of longer wave-length are slightly wider. The *i* band is considerably weaker than its neighboring bands.

Spectrograms (Plate 64, *A* and *B*) were made by exposing to the Nernst filament for 1 minute at 0.8 ampere, the slit-width being 0.08 mm. The spark was run about 3 minutes. In *A* the concentrations were 1.5, 1.125, 0.75, 0.5, 0.375, 0.25, and 0.1875 normal; in *B*, 0.1875, 0.14, 0.094, 0.0625, 0.047, 0.0312, and 0.0234 normal, starting in each case with the strip next to the spark-spectrum. The corresponding depths of cell were 3, 4, 6, 9, 12, 18, and 24 mm. respectively. In the case of the more concentrated solutions Beer's law was not found to hold. In *A* there appear the two wide absorption bands. The large wave-length limit of the ultra-violet band is independent of the concentration when the amount of salt is kept constant, and is located at about λ 3520. The blue-violet band on its short wave-length side also obeys Beer's law and ends at λ 3860. The long wave-length edge, however, is pushed towards the red as the concentration is increased; or, in other words, the absorption is greater for a given amount of salt in concentrated solutions than it is in dilute solutions. The positions of this edge for various concentrations are λ 4100 for 0.1875, 0.25, 0.375, and 0.5 normal; λ 4150 for 0.75 normal; λ 4300 for 1.125 normal; and λ 4340 for 1.5 normal. For *B* Beer's law holds and only the ultra-violet absorption band appears; its long wave-length side being at λ 3350. The intensities of the small bands are independent of concentration as far as one can tell from the spectrograms.

ABSORPTION SPECTRUM OF URANYL NITRATE CRYSTALS.

For the aqueous solution there is no sign that the bands can be broken up. In the spectrum of the crystal this is not the case. The *a* band is narrow. The *b* band is also very narrow, about 15 Ångström units wide. A very faint band appears about λ 4650. The *c* band, on the other hand, is very wide, about 70 Ångström units, and is probably double. The *d* band is about 50 Ångström units wide, and the *e* band is about 70 Ångström units wide and appears double. The *f* band is the most intense and is about 40 Ångström units wide. The bands *g*, *h*, *i*, and *j* keep decreasing in intensity respectively. The description is of a spectrogram taken of a crystal in Canada balsam, and of course the width of the bands varies with the time of exposure and various other things, but many details are shown that are not exhibited in other spectrograms. It will thus be seen that the *a*, *b*, *c*, *d*, *j*, and *k* bands of the solution agree fairly well with those of the crystal, and that the crystal bands *f*, *g*, *h*, and *i* are shifted towards the red with reference to the bands in the aqueous solution.

Effect of Dilution on the Uranyl Bands.

The effect of dilution on the position and intensity of the blue-violet, the ultra-violet, and the uranyl bands of the acetate, nitrate, and sulphate of uranyl in water was tried. The absorption spectra of solutions about 1 normal and 3 mm. deep were photographed along by the side of the absorption spectra of 0.008 normal solutions of the same salts 380 mm. deep. The absorption consisted of the blue-violet band, the ultra-violet band, and the *a*, *b*, *c*, *i*, *j*, and *k* bands. Between the blue-violet and ultra-violet bands there was the transmission band containing *i*, *j*, and *k*. For each of the three salts this transmission band was much weaker for the dilute solution, whereas in the cases of the sulphate and nitrate the long wavelength transmission edge of the blue-violet band was stronger for the more dilute solution. The opposite was true of the acetate solution. In the dilute solution of the acetate the bands were more intense than for the more concentrated solution. There was no noticeable change in the position of the bands. Neither the intensity nor the position of the uranyl nitrate or the uranyl sulphate bands was changed by the above dilution.

Plate 65, *A*, represents the spectrogram comparing the spectra of the same amount of uranyl salt in a concentrated and in a dilute solution. Starting with the strip adjacent to the numbered scale we have the absorption spectra of a 1.1 normal solution of uranyl nitrate in water, the depth of the cell being 3 mm. The next spectrogram is of the same solution. Then distilled water was poured into the solution until the length of column was 380 mm. The absorption spectrum of this solution is given in the third strip. The fourth strip represents the absorption of a 0.75 normal solution of uranyl sulphate, the depth of cell being 4 mm. The fifth strip is for the same solution diluted until the depth was 380 mm. The sixth strip represents the absorption of a 0.188 normal solution of uranyl acetate 14 mm. deep. The last strip is for the same solution diluted to a depth of 380 mm.

A more detailed study was made as to whether Beer's law holds for uranyl nitrate and for the other uranyl salts. The method of taking the spectrograms is the same as that used for the potassium salts.

Beer's law was found to hold for dilute solutions of uranyl nitrate in water. When the concentration is greater than 0.5 normal the absorption is greater than it should be if Beer's law held.

Uranyl Nitrate in Nitric Acid.

Ordinary uranyl nitrate ($UO_2(NO_3)_2 6H_2O$) was dissolved in very strong nitric acid. A spectrogram (Plate 70, *B*) was made of this solution, different depths of cell being used.

The presence of strong nitric acid has a very great effect upon the absorption spectra of uranyl nitrate. In general, it causes the band absorption to be very much more intense. The bands are shoved towards the violet. The *a* band, λ 4790, is made very weak, the *b* band, λ 4670, narrow and strong, the *c* band, λ 4510, the *d* band, λ 4370, and the *e* band, λ 4230, are quite strong. The other bands, *f*, λ 4125, *g*, λ 4000, *h*, λ 3900, *i*, λ 3790, *j*, λ 3670, and *k*, λ 3570, are rather weak, the latter two being stronger, however, than in the corresponding aqueous solution.

When the depth of layer is sufficient so that the whole shorter wave-length portion of the spectrum is absorbed to λ 4850, it is found that the whole region of the spectrum remaining is filled with a multitude of extremely fine absorption lines.

This fine band absorption spectrum is that of nitric oxide.

URANYL NITRATE IN METHYL ALCOHOL.

In a spectrogram the depth of cell was kept constant at 15 mm.; the concentrations, beginning with the strip nearest the scale, were .20, .158, .124, .10, 0.079, 0.063, and 0.05 normal. Exposure was made to the Nernst glower for 1 minute with the current at 0.8 ampere. The corresponding limits of absorption are λλ 4800, 3750, 3700, 3650, 3600, 3550, and 3500. Two of the smaller bands, *a* and *b*, appear at the lower concentration. These bands are about 30 Ångström units wide and their positions are λλ 4920 and 4745.

Plate 67, *B*, represents the same concentrations, 0.2 normal, as Plate 54, *A*. Here the depth of cell is kept constant at 3 mm. The spectrogram shows the characteristic blue-violet band and the ultra-violet band. For concentration 0.2 normal, the positions of the edge of the ultra-violet band are λλ 3825, 3800, 3770, 3750, 3720, 3700, and 3670.

The blue-violet band for 0.2 normal solution has the limits λ 4470 and λ 3825. The middle of this band thus comes at about λ 4150; exactly where the band for water is situated. The concentration when the same band fades out for water is 0.5 normal, whereas for alcohol it is much less, showing that uranyl salts in alcohol are much more deeply colored than in water. The following are the wave-lengths of the small bands: *a*, λ 4930; *b*, λ 4760; *c*, λ 4610; *d*, λ 4460; *e*, λ 4325; *f*, λ 4190; *g*, λ 4070; *h*, λ 3970; *i*, λ 3855.

For Plate 67, *A*, the Nernst glower was run 1 minute at 0.8 ampere, slit-width 0.08 mm. Starting with the comparison spectrum the concentrations were normal 0.2, 0.16, 0.126, 0.1, 0.08, 0.063, and 0.033, the corresponding depths of solution being 6, 7.5, 9.5, 12, 15, 19, and 24 mm. Uranyl nitrate in methyl alcohol shows very marked deviations from Beer's law, the absorption being much greater where the concentrated solutions are used. The limits of absorption for concentrations 0.2, 0.16, 0.126, 0.1, 0.08, 0.063, and 0.033 normal are, respectively, λλ 4720, 4700, 4680, 4660, 4650, 4640, and 4630.

URANYL NITRATE IN METHYL ALCOHOL AND WATER.

In the previous work of Jones and Anderson it was found that in the case of neodymium salts the absorption spectrum was very often different in pure alcohol from what it was in pure water. This fact had been noticed before by several observers, and had been believed by some to be due to the different dielectric constant of the two different solvents. According to such a theory the bands should gradually shift in position as one solvent was increased and the other decreased in amount. Jones and Anderson, however, found this not to be the case. They showed that *there was a definite set of methyl alcohol-bands and a definite set of water-bands.* As the amount of alcohol was decreased in a solution *the alcohol-bands weakened but remained in the same position. As the amount of water was increased the intensity of the water-bands increased, but they remained in the same position. These results were interpreted by them as being due to definite alcoholates and hydrates*—that a definite alcoholate of neodymium had a characteristic absorption spectrum. Recent work by E. E. Reid (Am. Chem. Jour., June, 1909) supports this theory. It should also be noticed that in general the alcohol-bands are on the red of similar water-bands.

One of the purposes of the present work was to find whether this matter of a salt possessing a characteristic absorption spectrum in different solvents was general or not. So far, it would seem to hold for uranyl nitrate. We have seen that uranyl nitrate bands in methyl alcohol are all nearer the red end of the spectrum than the corresponding water-bands. This is not in agreement with the results of previous investigators. To illustrate this we will give a table from Deussen's paper.[1]

Absorption spectra of uranyl nitrate in mixtures of water and methyl alcohol (Deussen).

Band.	Water.	50 per ct. CH_4O.	80 per ct. CH_4O.	100 per ct. CH_4O.	Band.	Water.	50 per ct. CH_4O.	80 per ct. CH_4O.	100 per ct. CH_4O.
a	4860	4860	4860	4850	*f*	4150	4155	4150	4090
b	4720	4720	4720	4680	*g*	4020	4030	4020	4000
c	4540	4540	4540	4490	*h*	3870	3875	3870	3840
d	4380	4385	4380	4360	*i*	3790	3800	3790	3750
e	4290	4295	4290	4295	*j*	3690	3690	3690	3660

The general results of Deussen are very surprising indeed. In general, he finds that by adding a little alcohol to an aqueous solution there is a slight shift of the uranyl nitrate bands to the red. The position of the bands then remains about the same with increasing percentage of alcohol until the solvent becomes almost pure alcohol, when there is a sudden shift towards the violet. In our work we find nothing of this kind. We find that in pure alcohol the bands are all shifted to the red as compared with the water-bands. In order to study further these bands, and to learn whether there was a gradual shift from alcohol-bands to water-bands, or whether the alcohol-bands simply became fainter but remained in the same position while the water-bands became stronger while remaining in the same position as the percentage of water was increased, a set of solutions was made up with varying amounts of water and alcohol; the concentration of uranyl nitrate remaining constant at 0.1 normal. For this purpose, of course, the anhydrous uranyl nitrate was used. Plate 66 represents two of the spectrograms. In *A*, starting with the strip nearest the spark-spectrum the percentages of alcohol were 100, 92, 84, 76, 68, 60,

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[1] Ann. Phys., **66**, 1132 (1898).

50. In *B* everything was the same excepting the depth of cell which was 6 mm., whereas in *A* it was 15 mm. An exposure of 1 minute was made to the Nernst glower running with a current of 0.8 ampere. The slit-width was 0.08 mm.

The original negatives show that the *absorption is much greater for the pure alcoholic solutions than for the mixtures with water.* The change from the absorption of pure alcohol to a 92 per cent solution is very marked. The plates show that *in mixtures of alcohol and water the bands are very broad, and that these broad bands are certainly the water- and alcohol-bands coexisting.* Their combination causes the banded appearance of the spectrum to be so weak that no measurements were made.

URANYL NITRATE IN ETHYL ALCOHOL.

The general absorption of uranyl nitrate in ethyl alcohol is similar to the absorption in methyl alcohol. Plate 68, *B*, represents the absorption of a 15 mm. solution, the concentrations being 0.2, 0.16, 0.127, 0.10, 0.08, 0.063, and 0.033 normal; the most concentrated solution being nearest the comparison scale. The source of light was the Nernst filament for 1 minute, at 0.08 ampere, with a slit of 0.08 mm. width. The characteristic wide absorption bands of uranyl, the blue-violet and the ultra-violet bands, merge together in the strips next to the comparison scale. They become separated at a concentration of 0.127 normal. The limits of the blue-violet band are for 0.1 normal λλ 4000 and 4670, for 0.08 normal λλ 3950 and 4550, for 0.063 normal λλ 3900 and 4500, for 0.033 normal λλ 3950 and 4450, the middle of the band coming at about λ 4200.

The characteristic uranyl bands of the ethyl alcohol solution are extremely faint, and on this account are hard to recognize. There is a wide and very faint band at λ 5200, which is at least 50 Ångström units wide, and has never been seen by the authors for any other uranyl salt. The band that comes approximately in the position of what we called band *a* is very wide, about 90 Ångström units. Band *b* is very faint. The following are the wave-lengths of the various bands, and we will designate them by small letters; although it is not certain whether say band *c* or *d* corresponds to bands that we have hitherto designated in this manner: *a*, 5000; *b*, 4800; *c*, 4630; *d*, 4475; *e*, 4325; *f*, 4175; *g*, 4080; *h*, 3970; *i*, 3875. Here again we obtain entirely different results from Deussen. He found that by gradually increasing the percentage of alcohol he first obtained a shift of the bands toward the red, and when the amount of alcohol kept on increasing a final shift towards the violet.

Starting with the comparison spectrum in Plate 68, *A*, the concentrations are 0.2, 0.16, 0.127, 0.10, 0.08, 0.063, and 0.033 normal, the corresponding depths of cell being 6 mm., 7.5 mm., 9.5 mm., 12 mm., 15 mm., 19 mm., and 24 mm. From the spectrogram it is seen that Beer's law does not hold, the absorption being greatest for the most concentrated solution. This holds true both for the blue-violet band and for the ultra-violet band. It would be interesting to know whether for the same dissociation Beer's law would hold for water and alcohol solutions; also whether other properties, like fluidity, vapor-pressure lowering, conductivity, etc., vary in the same way.

URANYL NITRATE IN MIXTURES OF GLYCEROL, WATER, ACETONE, AND ETHYL ALCOHOL.

Plate 69, *A* and *B*, represents the absorption of solutions 25 and 6 mm. in depth, respectively. Strip 1 represents the absorption of a solution of uranyl nitrate in glycerol; strip 2 of 3 parts glycerol and 1 part water; strip 3 of 2 parts glycerol and 2 parts water; strip 4 of 1 part glycerol and 3 parts water; strip 5 of 1 part glycerol and 3 parts acetone, and strip 6 of 1 part glycerol and 3 parts ethyl alcohol. The concentration of uranyl nitrate in glycerol was the same in each case.

	Strip 1, A B.	Strip 4, A B.	Strip 5, A B.	Strip 6, A B.
a	5040 5020	....	5000(*w*)	5080 5010 weak
b	4910	4880	4850	4860
c	4750	4710	4690	4710
d	One broad band	4560	4520	....
e		4440	4360	....
f	4350	4300	4220	....
g	4220	4160	4100	4090
h	4100	4030	3980	3970
i	3970	3900	3890	....
j	....	3800	3800	....
k	....	3700	3690	....

Plate *B* brings out clearly the fact that the addition of water causes the uranyl nitrate bands of glycerol to be gradually shifted towards the violet. The above identification of the acetone and methyl alcohol bands is open to correction.

URANYL NITRATE, TEMPERATURE EFFECT.

A spectrogram was made of a 0.0156 normal uranyl nitrate solution in water, the depth of layer being 196 mm. Exposures were made to the Nernst glower for 30 seconds, the current being 0.8 ampere and the slit-width 0.20 mm. The length of exposure to the spark was 4 minutes. Starting with the strip nearest the scale, the temperatures were 9°, 23°, 46°, 59°, 70°, and 79°.

At 9° the ultra-violet absorption band extended to λ 3430. Throughout the blue-violet band there was considerable transmission at this temperature, the stronger spark lines being only partially absorbed. The *a*, *b*, and *c* bands appeared, all being extremely weak, however, and in quite striking contrast with their strength in the aqueous solutions investigated in the earlier part of the work. Their wave-lengths were λλ 4550, 4705, and 4870.

As the temperature was raised, both the ultra-violet and the blue-violet bands widened. The intensity of the uranyl bands, on the other hand, did not seem to vary with the temperature. At 79° the ultra-violet band extends to λ 3550. The blue-violet band extends from λ 3900 to λ 4450. Only the *a* and *b* bands appear at this temperature, their positions being λ 4710 and λ 4875. There may be a slight shift towards the red, but if there is, it is too small in amount to be established with certainty.

Plate 71, *A*, represents the effect of rise in temperature on the absorption spectra of a $\frac{1}{64}$ normal solution of uranyl nitrate. From the fact that the uranyl nitrate bands have a shorter wave-length than the bands of the other salts, it was thought that the effect of temperature might be different; that at high temperatures all the bands might have the same positions. The uranyl nitrate bands shift very little to the red, if they shift at all, for changes in temperature of 90°. The effect of temperature seems to be independent of the temperature.

ABSORPTION SPECTRUM OF ANHYDROUS URANYL NITRATE.

When it was first discovered that the uranyl nitrate "water" bands were all shifted to the violet with reference to the band of the other uranyl salts in water, as well as with reference to the uranyl nitrate bands in other solvents, it was thought that possibly it was more hydrated than the other salts in solution. The uranyl salts crystallized from aqueous solutions at ordinary temperatures have the following composition: $UO_2(NO_3)_2.6H_2O$, UO_2SO_4-$3H_2O$, $UO_2(CH_3COO)_2.2H_2O$, and $UO_2Cl_2.H_2O$. This fact would favor the supposition that in solution the nitrate might be more hydrated than the other salts. The fact that the absorption of the aqueous solution of the nitrate and the crystallized salt was very much the same, as far as the positions of the uranyl bands is concerned, also seemed to favor this view.

In this connection it was considered important to examine the absorption spectrum of the anhydrous uranyl nitrate. This salt was powdered and placed in a closed glass tube just above the slit of the spectroscope. The light of a Nernst glower was then focused upon the surface of the salt nearest the slit and an exposure of about 3 hours made. In this way we examine light that has penetrated a short distance into the powder and is then diffusely reflected.

The absorption spectrum was found to consist of quite a large number of bands that seem quite different in many respects from those of the solution. The following are the approximate wave-lengths: $\lambda\lambda$ 4800, 4650, 4500, 4420, 4360, 4280, 4180 (broad), 4060 (broad), 3950 (broad), 3820 (broad), 3700 (narrow), and 3600 (narrow). The bands marked broad are from 50 to 60 Ångström units wide and the narrow bands about 20 Ångström units. If the first band is the *a* band, then the bands of the anhydrous salt are to the violet side of the corresponding bands of the crystals and of the solution. If it is the *b* band the opposite is the case. On account of the smallness of the intensity of the bands it could not be settled whether λ 4800 is the *a* or the *b* band. Further investigation of this point will be made.

There are two difficulties in the above theory, difficulties for which no explanation has thus far been suggested. In the work on the effect of rise in temperature on the absorption spectrum it was found that the uranyl nitrate bands did not shift to the red. On the other hand, the uranyl sulphate and uranyl chloride bands were shifted to the red under the same conditions. (In these cases aqueous solutions were investigated.) If the uranyl nitrate bands owe their position to a large amount of hydration, it would be expected that with rise in temperature they would be shifted towards the red more than the bands of the sulphate and chloride. Another difficulty is that of the effect of dilution. The greater the dilution the greater the dissociation, and, therefore, according to the theory of Arrhenius, for very dilute solutions the UO_2 group should exist in the ionic condition and the absorption spectrum of all the salts should be the same, *i. e.*, the uranyl bands should then occupy the same positions independently of the kind of salt. No effect of this kind is to be noticed, as was shown above under the division describing the effect of dilution. It is intended to use much more dilute solutions in the future.

URANYL BROMIDE IN WATER.

In Plate 72, *B*, we have the absorption spectra of uranyl bromide (crystalline salt, $UO_2Br_2.H_2O$). The exposures were 1 minute to the Nernst glower with 0.8 ampere and a slit-width of 0.08 mm., and a 3-minute exposure to the spark. The depth of the cell was 3 mm. and the concentrations were 1, 0.75, 0.5, 0.33, 0.25, 0.2, and 0.16 normal, the spectrum for the most concentrated solution being that next to the comparison spectrum.

It will be seen that uranyl bromide gives rise to an absorption very similar to uranyl nitrate, there being a blue-violet and an ultra-violet band. The absorption for the 1 normal solution is complete for all wave-lengths less than λ 4470. For 0.75 normal the limits of the blue-violet band are $\lambda\lambda$ 4450 and 3900, the ultra-violet band beginning at λ 3800. For 0.5 normal the blue-violet band shows considerably larger transmission, having almost completely faded out. Its middle comes at about λ 4250. The ultra-violet band gradually recedes towards the shorter wave-lengths as the dilution increases.

The uranyl bands themselves do not show nearly so prominently as in the case of the chloride and nitrate. The bands are very wide and diffuse. Their approximate positions are: *a*, 4880; *b*, 4720; *c*, 4560; *d*, 4450; *e*, 4280; *f*, 4160.

The spectrogram showing a series to test Beer's law is given in Plate 72, *A*. The concentrations, beginning with the strip nearest the numbered scale, are 1, 0.75, 0.5, 0.33, 0.25, 0.2, and 0.16 normal, the corresponding depths of cell being 3, 4, 6, 9, 12, 18, and 24 mm., respectively. Beer's law is found to hold, the limits of the absorption bands being independent of the above range of concentrations. The ultra-violet band and blue-violet band have a small region of transmission between them which shows in the original film but not on the print from it. This region of transmission is very faint and is quite a sensitive index to any possible deviations from Beer's law. It shows no changes in intensity with change in concentration. The uranyl bands *a* and *b* show, although they are very indefinite. Concentration does not affect their intensity in the least as far as can be detected.

URANYL SULPHATE, TEMPERATURE EFFECT.

A spectrogram (Plate 73, *A*) was made for a normal solution of uranyl sulphate, the depth of cell being 3 mm. The time of exposure was 90 seconds to the Nernst glower with a current of 0.8 ampere and a slit-width of 0.20 mm. The time of exposure to the spark was 6 minutes. Starting with the strip nearest to the numbered scale, the temperatures were 5°, 19°, 32°, 54°, 67°, and 84°.

The rise in temperature from 5° to 84° caused an encroachment of the ultra-violet band into the regions of greater wave-length. The blue-violet band increased in width, especially towards the red, as the temperature was raised. The uranyl bands themselves changed very slightly in intensity with rise in temperature.

At 5° the ultra-violet was absorbed to λ 3500. The blue-violet band extended from λ 3900 to λ 4400. The uranyl bands *a*, *b*, and *c* appeared at λλ 4570, 4730, and 4910.

At 84° the ultra-violet band extended to λ 3600, the blue-violet band from λ 3850 to λ 4550. The bands *a*, *b*, and *c* have become considerably more diffuse. Their positions are λλ 4590, 4745, and 4925, approximately.

A much more dilute solution (0.0156 normal) of uranyl sulphate (Plate 73, *B*), containing approximately the same amount of salt as the concentrated solution, was used. The length of cell in this case was 196 mm. The exposure was for 30 seconds to the Nernst glower (current 0.8 ampere, slit-width 0.20 mm.). The time of exposure to the spark was 4 minutes. Starting with the strip next to the comparison spectrum, the temperatures were 6°, 19°, 36°, 51°, 67°, and 81°.

At 6° the ultra-violet band extends to λ 3500 and the blue-violet band from λ 3950 to λ 4450. The positions of the *a*, *b*, and *c* bands are λλ 4565, 4720, and 4895. At 81° the ultra-violet absorption extended to λ 3600 and the blue-violet band from λ 3900 to λ 4500. The *a* and *b* bands were located at λλ 4735 and 4915. The effect of concentration on the temperature coefficient seems to be very small. In both concentrations, as the temperature was raised there was a slight shift of the uranyl bands to the red.

Several spectrograms were made in order to get the absorption spectra of the dry (anhydrous) uranyl sulphate. The bands were extremely faint, however, and no reliable measurements of their position could be made.

Uranyl Sulphate Mixed with Concentrated Sulphuric Acid.

Several spectrograms were taken to find whether the addition of very concentrated sulphuric acid to an aqueous solution of uranyl sulphate produced any effect. A normal solution was used—a spectrogram being taken of this solution. Very concentrated sulphuric acid was added until the length of the layer was 57.6 mm.; the concentration being then 0.052 normal. In both spectrograms the position of the long wave-length side of the blue-violet band remained the same. The bands *a* and *b* appear in both cases, and *c* rather faintly. In the aqueous solution *b* is about five times stronger than *a*. In the sulphuric acid mixture, however, *a* increases in intensity; *i.e.*, its absorption becomes greater; whereas *b* becomes considerably narrower, so that *a* and *b* have about the same intensity. The uranyl sulphate bands in the sulphuric acid solution resemble very closely the same bands for uranyl nitrate crystals.

In very strong sulphuric acid the bands of uranyl sulphate have the following wave-lengths: *a*, λ 4930, about 30 Ångström units wide; *b*, λ 4745, almost identical in character with *a*; *c*, λ 4550, about 80 Ångström units wide and appears sometimes to be double; *d*, λ 4380 (70 Ångström units); *e*, λ 4240 (70 Ångström units wide); *f*, λ 4100; *g*, λ 3980; *h*, λ 3870; *i*, λ 3770; *j*, λ 3660.

URANYL ACETATE IN WATER.

Uranyl acetate crystallizes from an aqueous solution at ordinary temperatures as $UO_2(CH_3COO)_2 2H_2O$. The aqueous solution of this salt is very similar to that of the uranyl salts previously described, showing the blue-violet and ultra-violet bands and also the characteristic uranyl bands. This salt in solution is much more highly colored for the same concentration than the nitrate or bromide.

Plate 74, *B*, represents the absorption of a series of solutions where the concentration was kept constant and the depth of layer varied. The usual procedure was to keep the concentration constant and vary the depth of cell. For salts obeying Beer's law this would give the same absorption as keeping the depth of cell constant and varying the concentration, so that in our spectrograms of a salt where Beer's law holds no difference is made between these two cases. Where Beer's law is deviated from, the two cases will not be identical. For the case under consideration the concentration was 0.031 normal and the depths of cell, starting with the strip nearest the numbered scale, were 24, 18, 12, 9, 6, 4, and 3 mm. The length of exposure to the Nernst glower with 0.08 ampere and a slit-width of 0.08 mm. was 1 minute.

The blue-violet band has the boundaries λλ 4500 and 4050 for a 24 mm. cell, and λλ 4400 and 4100 for a depth of 18 mm., the middle of the band thus coming at about λ 4250. The long wave-length edges of the ultra-violet band are λλ 3750, 3700, 3680, 3660, 3630, 3600, and 3580 for depths of cell of 24, 18, 12, 9, 6, 4, and 3 mm., respectively.

A photograph was made to bring out the small uranyl bands. An exposure was first made for 1 minute (0.08 ampere and 0.08 mm. slit) in the yellow end of the spectrum. This solution was 15 mm. deep in every case. The screen was interposed so as to cut off all light of greater wave-length than λ 4450. A long exposure to the Nernst filament—about 5 minutes—was then made. Another screen was then interposed which cut out all light of wave-length greater than λ 2800, and an exposure made to the spark. During these three exposures nothing was moved except the screen, and thus the question of any mechanical moving of the photographic film was eliminated. From these two plates the positions of 9 uranyl bands were measured. These were as follows: *a*, 4910(?); *b*, 4740; *c*, 4595; *d*, 4455(?); *e*, 4310; *f*, 4160; *g*, 4070; *h*, 3970; *i*, 3865.

It will be seen that these bands are all nearer the red than the bands of uranyl nitrate in water.

Deussen found the following values: *a*, 4875; *b*, 4730; *c*, 4575; *d*, 4420; *e*, 4310; *f*, 4180; *g*, 4060; *h*, 3950; *i*, 3860; *j*, 3770. These are in satisfactory agreement with the values given above.

The spectrogram, Plate 74, *A*, represents the change in absorption of uranyl acetate with concentration when the amount of salt in the path of the light beam is kept constant. The exposure was 1 minute to the Nernst glower, with 0.8 ampere (slit 0.08 mm.), and 3 minutes to the spark. Starting from the comparison spectrum the concentrations are 0.25, 0.185, 0.125, 0.083, 0.0625, 0.042, and 0.031 normal, the corresponding depths of cell being 3, 4, 6, 9, 12, 18, and 24 mm.

This uranyl salt shows a deviation from Beer's law which is different from the deviation of any salt previously studied. All other salts show, for a Beer's law series, a greater absorption at the greater concentration. Uranyl acetate shows the opposite, a greater absorption for the less concentrated solutions. For the 0.25 normal solution the blue-violet band extends from λ 4150 to λ 4250. At 0.031 normal it has broadened, so that its limits are λλ 4500 and 4050. This broadening of the absorption is gradual. In like manner the ultra-violet band extends to λ 4400 for the 0.25 normal solution and to λ 4300 for the 0.031 normal solution.

A 0.188 normal solution of uranyl acetate 14 mm. in length was diluted to 0.007 normal and 380 mm. in length. The absorption was found to be greater for the more dilute solution. The uranyl bands were not shifted and were much broader in the dilute solution.

Anhydrous Uranyl Acetate.

To determine whether the water of crystallization of uranyl acetate, $UO_2(CH_3COO)_2.2H_2O$, had any effect on the position of the uranyl acetate bands, the absorption of the anhydrous salt was found in the same way as for uranyl nitrate. Seven bands could be detected, but most of them were quite faint, although stronger than the bands of the nitrate: *a*, 4905; *b*, 4775; *c*, 4605; *d*, 4460; *e*, 4320; *f*, 4200; *g*, 4085. It will be seen that there is a slight shift towards the red as compared with the aqueous solution.

Uranyl Acetate in Methyl Alcohol.

For the uranyl acetate the exposure to the Nernst glower, with 0.8 ampere and a slit-width of 0.08 mm., was 1 minute. No exposure was made to the spark except for a comparison spectrum. Starting with the strip nearest the spark scale, in Plate 75, *B*, the concentrations were 0.25, 0.20, 0.16, 0.12, 0.10, 0.07, and 0.06 normal. The depth of cell was constant, 6 mm. The edges of the blue-violet absorption were as follows: 0.25 normal, λλ 4550 and 3850, 0.20 normal, λλ 4520 and 3900, 0.16 normal λλ 4500 and 3950, and 0.12 normal λλ 4550 and 4000. The middle of the band would thus come at about λ 4270. As the spark was not used the exact edges of the ultra-violet band can not be given.

The uranyl bands had the following positions: *a*, 4875; *b*, 4720; *c*, 4585; *d*, 4445; *e*, 4320; *f*, 4185; *g*, 4070; *h*, 3975.

A plate was made to test Beer's law. Starting with the strip nearest the comparison scale the concentrations were 0.25, 0.20, 0.16, 0.12, 0.10, 0.07, and 0.06 normal, the corresponding depths of cell being 6, 7.5, 9.5, 12, 15, 19, and 24 mm. The deviation from Beer's law is the same in direction as for uranyl acetate in aqueous solution and is not nearly so great. For the 0.25 normal solution the limits of the blue-violet band were λλ 4470 and 3925, the distance between the blue-violet band and the ultra-violet band at this concentration being about 100 Ångström units. For the 0.06 normal solution the blue-violet and ultra-violet bands have completely merged and the limit of absorption is about λ 4600.

THE URANYL BANDS OF THE ACETATE.

The following table gives the approximate wave-lengths of the uranyl bands of the acetate in water and in methyl alcohol, and of the anhydrous powder:

Bands of uranyl acetate.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
Water............	4910	4740	4595	4455	4310	4160	4070	3970	3830
Methyl alcohol.....	4880	4720	4590	4450	4320	4190	4070	....	....
Anhydrous salt.....	4910	4780	4610	4460	4320	4200	4090	3980	....

From this table it seems that the positions of the bands of the acetate under these different conditions are about the same.

URANYL ACETATE, TEMPERATURE EFFECT.

A spectrogram showing the effect of rise in temperature was made for a 0.0039 normal aqueous solution of uranyl acetate 196 mm. deep. The exposures were made for 30 seconds to the Nernst glower, with a current of 0.8 ampere and a slit-width of 0.20 mm. No exposure was made to the spark at all. The temperatures, starting with the strip nearest the comparison spectrum, were 6°, 18°, 30°, 43°, 56°, 68°, and 75°.

The spectrogram shows the ultra-violet and blue-violet bands common to all uranyl salts. The transmission band between these absorption bands is about 200 Ångström units wide and changes very little with change in temperature. The blue-violet band advances rapidly towards the red as the temperature rises. At 6° the blue-violet band extends from λ 3950 to λ 4500. The latter edge gradually runs towards the red until at 75° it is about λ 4600. The uranyl bands *a* and *b* appear. They are very weak and gradually shift towards the red with rise in temperature.

SPECTROPHOTOGRAPHY OF CHEMICAL REACTIONS OF URANYL SALTS.

Plate 81, *B*, represents the absorption spectrum of a solution 15 mm. in depth and containing an 0.08 normal solution of a uranyl salt in water. Beginning with an 0.08 normal solution of uranyl nitrate, sulphuric acid was added so as to make the concentration of acid beginning with strip 1 as follows: 0.37, 0.73, 1.46, 2.92, 5.84, 10.22, and 14.60 normal.

It will be seen that in strip 1 we have practically the sulphate spectrum, most of the nitrate having been transformed. The addition of more acid does not produce any marked change until we reach the sixth and seventh strips. Here we see that the *c* and *d* bands are very greatly shifted, so that in the latter strip they form a single band. Several of the other bands are considerably shifted towards the red. Throughout the changes of conditions above named, the bands remain quite sharp and well defined (for uranyl bands), and change very little in intensity. This is in quite marked contrast with many of the plates in which there are certain stages that hardly show any uranyl bands at all, whereas at other stages the bands will be very strong indeed.

The bands in the upper strips beyond the region λ 5000 are probably due to nitric oxide. Several of the bands are quite strong.

	Nitrate bands.	Sulphate bands.	Strip 1.	Strip 5.	Strip 6.	Strip 7.
				5230? 5200? 5170? 5100? 5000?		
a	4890 4800	4900	4900 to 5100	4910	4920	4920
b	4742 4722	4740	4730	4750	4740	
c	4540	4580	4570	4570	4570 4480	4550
d	4390	4460	4440	4450		
e	....	4330	4320	4340	4340	4370
f	4155	4200	4200	4200	4210	4225
g	4030	4070	4070	4070	4080	4090
h	3905	3970	3950	3970	3960	3970
i	3815	3850	3850	3850	3860	3860
j	3710	3740	3720	3740	3750	3760
k	....	....	3620	3620	3640	3650
l	3515	3530	3520	3520	....	....

The simplest interpretation of this plate is that as more and more sulphuric acid is added molecules are formed that contain more and more of the acid. That there are several of these compounds formed seems probable, since the shift of the bands is quite large and this shift takes place gradually.

	Nitrate bands.	Chloride bands.	Strip 1.	Strip 6.	Strip 7.
a	4890 4800	4920			
b	4742 4722	4740	4700 weak and broad	4720	4740
c	4540	4560	4560 weak and broad	4580	4580
d	4390	4460	4410 weak and broad	4430	4440
e	....	4315	4270 strong	4280	
f	4155	4170	4140 strong	4145	
g	4030	4025	4020 strong	4020	
h	3905	....	3900	3900	3900
i	3815	....	3800	3800	
j	3710	....	3700	3700	3700 weak
k	....	....	3600	3600	3600 weak
l	3515	....	3500	3500	

Plate 83, *A*, gives the effect of adding sulphuric acid to an aqueous solution of uranyl nitrate. The first strip here gives the absorption of uranyl nitrate to which no acid has been added. The changes here are from the neutral nitrate bands to the neutral sulphate bands, approximately. There is in this case a gradual shift of the bands to the red.

Plate 79, *B*, represents the effect of adding hydrochloric acid to an aqueous solution of uranyl nitrate. The depth of cell was 15 mm. The concentration of the uranyl salt was kept constant. The percentages of acid were increased.

In the first strips the *b* and *c* bands are very weak. They become stronger and shift gradually to the red. The other bands are quite sharp until the last strip, where they appear very weak. Their wave-lengths are but slightly changed. In the above table the wave-lengths of the neutral chloride and nitrate bands are taken from the other tables. Strip 1 of this plate and strip 1 of Plate 81, *B*, are entirely different.

Plate 83, *B*, represents the absorption spectra of uranyl nitrate to which acetic acid had been added. Plate 82, *A*, represents the same effect, except that here the original uranyl nitrate solution was only 1 mm. in thickness; so that the ratio of acetic acid to the amount of uranyl salt was much larger.

	Uranyl nitrate.	Strip 1. Plate 83, *B*.	Strip 6. Plate 83, *B*.	Strip 1. Plate 82, *A*	Strip 3. Plate 82, *A*.	Strip 5. Plate 82, *A*.	Uranyl acetate.
a	4890 4800	4830?					
b	4742 4722	4660	4675			4860	4900
c	4540	4510	4520		4650	4720	4770
d	4390	4370	4380	4420 weak	4500	4570	4600
e	....	4245	4250	4270	4350	4440	4460
f	4155	4130	4140	4150	4220	4340 4220	4320 4200
g	4030	4020	4030	4020	4030	4120	4090
h	3905	3910	3920	3910	3910	4010	3975
i	3815	3800	3810	3800		3870	
j	3710	3670	3700	3700		3770	
k	....	3570	3580	3600		3670	
l	3515	3460	3460				

The first effect which the addition of acetic acid produces is to shift slightly the uranyl bands of the nitrate to the red, and to cause them to become much sharper. When some twenty times as much strong glacial acetic acid had been added as was equivalent to the uranyl nitrate solution, the uranyl bands became quite weak, and shifted very greatly towards the red, as is shown in Plate 82, *A*. The *e* and *f* bands are each shifted nearly 200 Ångström units. When this enormous shift towards the red takes place a *new* band appears between *f* and *g*. This new band will be called f_1. Further addition of acetic acid causes the uranyl bands to become stronger again, producing at the same time a small shift to the red.

URANYL CHLORIDE IN WATER, CONDUCTIVITY AND TEMPERATURE COEFFICIENTS.

Uranyl chloride, like other uranyl salts, is strongly hydrolyzed in dilute solution.

V.	35°.	50°.	65°.	Temperature coefficients.			
				35° to 50°.		50° to 65°.	
	μv	μv	μv	Cond. units.	Per cent.	Cond. units.	Per cent.
4	220.4	274.6	333.2	3.61	1.64	3.91	1.42
8	253.5	318.9	387.8	4.36	1.72	4.59	1.44
32	301.4	380.3	473.2	5.26	1.74	6.19	1.63
128	342.0	439.4	548.5	6.49	1.90	7.27	1.65
512	379.4	491.1	610.6	7.45	1.96	7.97	1.62
2048	418.5	546.8	693.7	8.55	2.04	9.79	1.97

URANYL NITRATE IN WATER, CONDUCTIVITY AND TEMPERATURE COEFFICIENTS.

The salts of uranium, like the salts of chromium, undergo hydrolysis at the higher dilutions, and the dissociations, therefore, can not be calculated.

V.	35°.	50°.	65°.	Temperature coefficients.			
				35° to 50°.		50° to 65°.	
	μv	μv	μv	Cond. units.	Per cent.	Cond. units.	Per cent.
4	176.0	220.1	268.3	2.94	1.67	2.21	1.46
8	199.2	251.2	307.1	3.46	1.74	3.73	1.48
32	233.8	298.0	372.0	4.28	1.83	4.93	1.65
128	275.4	354.6	444.7	5.28	1.92	6.01	1.69
512	303.2	395.8	502.0	6.17	2.03	7.08	1.79
2048	349.0	460.8	585.3	7.45	2.13	8.30	1.80

URANYL SULPHATE IN WATER, CONDUCTIVITY AND TEMPERATURE COEFFICIENTS.

The temperature coefficients in per cent, as with uranyl acetate, decrease with increase in dilution.

V.	35°.	50°.	65°.	Temperature coefficients.			
				35° to 50°.		50° to 65°.	
	μv	μv	μv	Cond. units.	Per cent.	Cond. units.	Per cent.
16	90.10	110.5	131.3	1.36	1.51	1.39	1.26
32	115.9	139.5	162.8	1.57	1.35	1.55	1.11
128	155.0	185.0	213.7	2.00	1.29	1.91	1.03
512	219.0	264.3	303.7	3.02	1.38	2.63	0.99

Uranyl Acetate in Water, Conductivity and Temperature Coefficients.

It will be seen that the temperature coefficients expressed in per cent decrease with increase in the dilution. This is rather unusual; these coefficients, as a rule, increasing with the dilution.

V.	35°.	50°.	65°.	Temperature coefficients.			
				35° to 50°.		50° to 65°.	
	μv	μv	μv	Cond. units.	Per cent.	Cond. units.	Per cent.
16	48.06	59.34	71.36	0.75	1.56	0.80	1.34
32	54.92	67.36	80.47	0.83	1.51	0.87	1.29
128	72.26	87.65	103.40	1.02	1.41	1.05	1.19
512	92.92	111.30	130.00	1.22	1.31	1.25	1.12
2048	118.40	141.40	165.40	1.53	1.29	1.60	1.13

The Phosphorescent and Fluorescent Spectra of Uranyl Salts.

Many bodies on being exposed to light, X-rays, α, β, γ, or cathode rays, on being heated or rubbed, emit light. This is generally called phosphorescence when the light is emitted after the stimulating agent ceases to act, and fluorescence when the excited light ceases to be emitted as soon as the exciting cause ceases. In general, liquids and gases fluoresce while solids phosphoresce. Some of the strongest phosphorescent compounds are the uranyl salts. These salts emit bands of phosphorescent light in the green region of the spectrum.

The researches of Lecocq de Boisbaudran, Lenard and Klatt, Urbain, and others, upon the rare earths, the sulphur compounds of the alkaline earths, and the oxides of the earth metals, have shown that these substances do not phosphoresce when in the pure state, and that the presence of an impurity seems to be essential to the formation in those substances of the complex molecules or "centra" that emit the phosphorescent light. On the other hand, the uranyl salts always phosphoresce.

Lenard and Klatt[1] have investigated very thoroughly various calcium phosphates of bismuth, manganese, and nickel. At ordinary temperatures the bands are very broad, ill-defined, and are unaffected by a magnetic field. Lenard and Klatt believe that there are certain places in atoms that can store electrons. These dynamids are only supposed to hold the electrons at low temperatures. At high temperatures the electrons possess a much greater freedom of motion. The different states of motion are visualized as three kinds: the "gaseous," "liquid," and "solid" states. In the "gaseous" state the electrons can occasion the conduction of electricity between the atoms if the latter exist in the same way as they do in metals. In the "liquid" state the electrons are in a state of motion sensitive to light vibrations and, hence, they take part in light absorption. In the "solid" state the electrons take part neither in conduction nor in

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[1] Ann. Phys., **15**, 225, 451, 633 (1904).

absorption. At low temperatures the spheres of influence of the dynamids are considered to extend to greater distances than at high temperatures, and the free paths of the electrons are also greatly reduced.

To each phosphorescent band Lenard and Klatt assign three phases: An upper momentary or heat phase; a permanent phase possessing quite definite temperature limits; and a lower momentary or cold phase. These phases succeed each other as the temperature falls. The upper momentary phase results when the dynamids do not store electrons. Whenever electrons are stored, these return afterwards to the atom from which they were expelled by the light-wave, and produce the permanent phase of the phosphorescent band. At low temperatures a few electrons return to the atoms from which they were expelled and these cause the lower momentary phase.

In general the temperature of solid hydrogen is sufficiently low to bring all phosphors into the lower momentary phase. Lowering the temperature to —180° continually causes new bands to appear in the permanent phase. Among such bands of long duration, for example, is the Ca.Niβ band, or the orange afterglow of BaCu. According to Lenard and Klatt uranyl compounds show only the upper momentary phase.

There are definite wave-lengths which in all temperature phases of the centra bring into phosphorescence only the momentary phase. The electrons under the photoelectric influence of these wave-lengths are ejected from the metallic atoms of the centra, and then return almost immediately to the metallic atom again; thus causing the emission of light. Other wave-lengths cause the electrons to be ejected from the same centra, but in this case the electrons are retained in the neighborhood. These stored electrons, when they finally return to the atom from which they were ejected, produce the phosphorescent band of the permanent phase.

The phenomena of luminescence are generally conceded to be due to some kind of electrolytic dissociation or ionization of the dissolved substance in the medium about it. Among the first to hold this view were Wiedeman and Schmidt.[1] The theory explains Stokes' law [2] and most of the other properties of phosphorescence. Some of these other properties are as follows: The distribution of intensity throughout a phosphorescent band is independent of the intensity and the wave-length of the exciting light; the light emitted from an isotropic medium is unpolarized; during the decay of phosphorescence each band behaves as an individual unit; the decay curve is dependent on the intensity and duration of excitation; the behavior of a phosphorescent body depends upon its past history.

Wiedeman and Schmidt have suggested that some of the ions produced during phosphorescent excitation form semi-stable combinations with the solvent molecules, and that after excitation these combinations are broken down. Merritt [3] further discusses the theory of Wiedeman and Schmidt.

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[1] Ann. Phys., **56**, 177 (1895).
[2] Phys. Rev., **22**, 279 (1906).
[3] *Ibid.*, **27**, 384 (1908).

He considers that the first effect of the exciting light is to produce dissociation. This dissociation may be either chemical or electrolytic. Electrolytic dissociation may consist of a dissociation similar to that taking place in ordinary electrolysis, or in the expulsion of one or more electrons from the molecule. Suppose that an electron is expelled from the atom; the two resulting ions will then have very different mobilities. The electrons will only temporarily attach themselves to molecules on account of their great velocities. The positive ions, on the other hand, will much more likely attach themselves either to the solvent molecules or to other molecules of the active substance. For the reason that the mobility of the positive ion is small, Merritt considers that the combinations which it forms are much more stable than those formed by the electrons.

As there are different kinds of combinations present there will be different kinds of collisions, and it is in collisions and recombinations of this kind that one is to find the source of the light emitted during phosphorescence. The vibrations corresponding to the different modes of recombination will probably differ in violence, frequency, and radiating power.

Very important work has been done by Urbain[1] and others upon the phosphorescence of the rare earths. To each one of the elements of the rare earths there corresponds a definite atomic weight, definite arc and spark spectra, and definite absorption and phosphorescent spectra. The oxides of europium, gadolinium, terbium, dysprosium, etc., are not phosphorescent. Mixtures of these compounds are, however, extremely phosphorescent, and in general there is a certain proportion at which the phosphorescence is a maximum. For example, one part of the oxide of europium in two hundred and fifty parts of gadolinium gives a maximum europium phosphorescence. The phosphorescence in this case is due to the europium atom or molecule, and is not greatly affected by the diluent. However, different diluents as lime or gadolinium do show a slight effect upon the resulting spectra. The temperature of calcination and the acid radical of the diluent also have an influence. For mixtures of europium and calcium compounds there exist two different sets of bands possessing different optima. Mixtures of europium and gadolinium, calcined at 1000° C. and 1600° C., give entirely different phosphorescent spectra. Gadolinium is much more effective in exciting phosphorescence than calcium. The spectra of different diluents do not change into each other but remain fixed, the intensity being the only variable.

A considerable amount of work on the phosphorescence of uranyl compounds has been done by the Becquerels. E. Becquerel[2] found that the phosphorescent spectra of pure uranyl chloride and of double salts of uranyl and potassium or ammonium were quite different, and that apparently the presence of potassium and ammonium caused the bands to shift towards the longer wave-lengths. The wave-lengths of the bands as given by Becquerel are:

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[1] Compt. rend., **142**, 205; 1518; **143**, 229; **144**, 30; 1363; **147**, 1472. Soc. Fran. de Phys., Feb. 6 (1906); July 6 (1906); Le Radium, June (1909).

[2] Ann. Chim. Phys. [4], **27**, 539–579 (1872).

Phosphorescent bands.

	1.	2.	3.	4.	5.	6.	7.
Uranyl nitrate ...	6544	6180	5810 5860	5590	5325 5325	5090	4920
Uranyl acetate...	6525	6180	5860	5590	5325	5090	4920
Uranyl chloride ..	....	6230	5955	5685	5433	5176	4980
Uranyl sulphate..	6620	6262	5955	5690	5418	5170	4945

The bands of the nitrate and acetate come at about the same place in the spectrum, whereas the chloride and sulphate bands are farther towards the red. H. Becquerel[1] finds that at low temperatures the phosphorescent uranyl bands become quite sharp in the same way that absorption bands do. For uranyl nitrate he gives the following table:

Phosphorescent spectrum of uranyl nitrate.

Room temperature.	Liquid-air temperature.	Room temperature.	Liquid-air temperature.
6210–6150	6360	5360–5280	5327–5320(s)
	6175–6165		5303–5292(s)
	6145–6127		5272
	6104		5240
	6005–6045		5190
5940–5840	5860–5853(s)		5137
	5837–5830(s)	5120–5060	5115
	5782		5097–5090(s)
	5707		5074–5070(s)
	5630		5018
	5600		4975
5630–5550	5585–5575(s)		4925
	5558–5548(s)	4893–4855	4903–4896(s)
	5490		
	5435		
	5375		

Further work has recently been published by J. Becquerel and Onnes.[2] At the temperature of solid hydrogen the intensity of emission is not diminished and the bands which existed at liquid-air temperatures undergo further subdivision. Lowering the temperature shifts the emission bands towards the violet. For instance, for the double sulphate of uranyl and potassium:

80° K	4904.2	5114.8	5342.4	5590.9	5863.1
20° K	4903.4	5113.5	5341.0	5588.9	5860.5
	0.8	1.3	1.4	2.0	2.6

The displacement of the phosphorescent bands caused by lowering the temperature from 20° to 14° is very small, and it is quite possible that as the temperature is lowered the bands approach asymptotically a limiting

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[1] Compt. rend., **144**, 459–462 (1907).

[2] Commun. Phys. Lab., Univ. Leyden, Nos. **110**, **111**.

position. Becquerel and Onnes find that the difference in the appearance of the different groups of bands is the result of successive ascending changes in the relative intensities of the bands in these groups. They find, when crystals of double salts are used, that the spectrum depends more upon the acid of the salt than upon the other base. The difference between the frequencies of two successive homologous bands is practically constant, not only for the same, but also for all series of homologous bands of the same salt. The values of this constant for the various salts differ but slightly from one another.

At low temperatures the phosphorescent spectrum of uranyl compounds resembles that of the channeled spectrum of nitrogen and carbon. Becquerel and Onnes consider both to have the same character. Placing the phosphorescing uranyl salt in a powerful magnetic field did not produce any noticeable effect upon the uranyl bands. Some of the bands become arbitrarily absorption or emission bands, and at low temperatures the wave-lengths are the same for both kinds of bands. Following is a table giving the wave-lengths of the phosphorescent bands of various uranyl salts at 80° C.

The authors have done a little work on the phosphorescent spectra of uranyl compounds. For the stimulation of the phosphorescent bands either sunlight or the light from a spark has been used. The glass screens previously described or a Feuss monochromatic illuminator were used when only certain wave-lengths of exciting light were needed. In the case of uranyl nitrate it was found that practically no phosphorescence was excited unless the exciting light had a wave-length less than λ 4900. For all wave-lengths less than this phosphorescence was excited, but the bands seemed the same, irrespective of the wave-length of the exciting light. It seems that the energy that is absorbed by the series of uranyl absorption bands is partly radiated as the energy of the phosphorescent bands. This suggests a number of lines of work which we hope to carry out in the future. Among these are the following: Are the phosphorescent bands of the salts of uranyl affected in the same way as the uranyl absorption bands? In the case of uranyl chloride can phosphorescent light be excited by the bands in the region λ 6000? Does light of wave-lengths between that of the uranyl absorption bands excite phosphorescence? In the case of uranyl

Phosphorescent bands.

Double sulphate of uranyl and sodium	......	4891.5	5101.2	5330.0	5578.5		
	......	......	5125.4	5354.7	5604.6		
Double sulphate of uranyl and ammonium	......	4912.6	5124.5	5355.4	5607.4	5881.1	6184.0
	......	4934.7	5147.8	5380.1	5633.3	5908.0	6215.7
Uranyl sulphate	......	4918.3	5133.9	5369.4	5626.8	5910.1	6219.5
		......	5160.2	5395.8	5654.0	5938.8	......
Uranyl nitrate	......	......	5069.6	5301.5	5554.6	5832.9	......
Double acetate of uranyl and sodium	4732.5	4932.5	5148.6	5384.5	5642.7		
	......	4950.2	5167.8	5404.5	5663.4		
	4762.3	4964.9	5184.9	5424.0	5685.8		
	4769.2	4972.1	5192.2	5431.6	5694.6		
	4785.8	4990.2	......	......			
	4794.6	4999.2	5221.4	5463.5			

nitrate obtained from an alcoholic solution would light of wave-length greater than λ 4900 excite phosphorescence?

Different salts of uranyl phosphoresce very differently. The specimens of uranyl chloride gave very weak and diffuse bands. Uranyl nitrate obtained from the evaporation of a methyl alcohol solution showed no phosphorescence. Uranyl bromide also gave very little phosphorescent light on excitation. Using the Hilger spectroscope, the following approximate wave-lengths for bands of various salts were found:

Uranyl sulphate.........	5660	5580	5420	5315	5210–5160	5085	4950	4860
Uranyl nitrate..........	5670	5600	5410	5330	5180	5100	4970	4840
Uranyl acetate..........	....	5570	....	5340	....	5070	....	....

The bands are so hazy and wide that these measurements mean very little.

Very little has been done on the fluorescence of solutions of uranyl salts. Some work by Stokes, Becquerel, Morton and Bolton, and others treats of fluorescent bands. Morton and Bolton give the following wave-lengths for some of the fluorescent bands of the solid salts:

Uranyl acetate, solid..........	6240	6070	5760	5500	5240	5030	....	....
Uranyl chloride, solid..........	6300	6000	5660	5400	5180	4930	....	....
Uranyl monophosphate, solid...	6510	6170	5850	5600	5200	5100	4880	4720
Uranyl monophosphate, in solution......................	6470	6200	5910	5650	5380	5160	4920	4800
Uranyl sulphate..............	6520	6150	5870	5600	5340	5110	4890	4770
Uranyl sulphate, anhydrous. ...	6580	6230	5930	5630	5365	5145	4850	4780

URANOUS SALTS.

Uranium was discovered in 1789 by Klaproth and was named to commemorate the discovery of the planet Uranus by Herschel in 1781. Quite a large number of oxides are known.

The orange oxide, $UO_3(UO_2O)$, or uranyl oxide is obtained by heating uranyl nitrate slowly as long as acid fumes escape. When the nitrate is rapidly decomposed a red modification of the oxide is produced. All the uranyl salts may be considered as compounds of UO_3, where one of the oxygen atoms has been replaced by an acid or halogen radical. Aqueous solutions of the uranyl salts are partly hydrolyzed. The non-hydrolyzed portion dissociates in the usual way.

Urano-uranic oxide (U_3O_8) is obtained by heating uranyl nitrate to a high temperature.

The oxide UO_2 is obtained by heating U_3O_8 in a current of hydrogen, and is of a brown or copper-red color. The reduction of an oxide of uranium to UO_2 and weighing is an analytical method of estimating uranium. This oxide in acid solutions forms the green uranous salts.

The oxide U_2O_5 is formed when ammonium uranate is strongly ignited in air. UO_4 is formed when a dilute solution of hydrogen peroxide is added to uranyl nitrate. The uranates have the general formula $R_2U_2O_7$, as, for example, potassium uranate, $K_2U_2O_7$. When alcohol is added to a solution of hydrogen peroxide, uranyl nitrate, and potassium hydroxide (a minimum amount of the hydroxide), golden yellow needles crystallize out having the composition $(NaO_2)_2UO_4.8H_2O$.

Very little work has been done up to the present on the absorption spectra of uranous salts, largely because of their very unstable character in solution. J. Formánek[1] describes the absorption spectra of uranous chloride. This was prepared by adding a little zinc and hydrochloric acid to a uranyl chloride solution. He found that the spectrum changed as the uranyl chloride was being reduced. A very strong band was found at λ 6507. The other bands, eleven in number, were λλ 6722, 6367, 6165, 6030, 5782, 5497, 5238, 5064, 4962. 4840, and 4519.

A similar method has been used by the writers. The uranous nitrate, sulphate, and chloride were formed by adding the corresponding acid to a solution of the uranyl salt containing some zinc. The uranous chloride and sulphate were quite stable in solution, remaining reduced for weeks. Uranous sulphate crystallizes out from solution as $U(SO_4)_2.9H_2O$. Solutions in alcohol can be reduced just as easily as solutions in water. Uranous nitrate was found to be very unstable. At the present writing a number of spectrograms have been made, and much more work will be done on these uranous salts and on the absorption spectra of the various oxides. It has already been found that uranous chloride[2] has very different spectra in different solvents.

URANOUS CHLORIDE IN WATER.

A solution of uranous chloride in water was made in the usual way. This solution was of a dark green color even when very dilute. When sufficiently dilute most of the uranous salt came down as a precipitate after standing for several days. The solution was examined spectroscopically it being practically colorless to the naked eye. The absorption spectra corresponded closely to that of the uranyl chloride bands of water. *e*, *f*, and *g* appear with considerable intensity, while the other bands are very weak; *e* consisting of two bands of about equal intensity and very close together. The wave-lengths of the bands are approximately as follows: λ 5030 (weak); *a*, λ 4910; *b* (very weak), λ 4790; *c* (very weak), λ 4550; *d* (very weak), λ 4420; *e*, λλ 4305, 4270; *f*, λ 4150, and *g*, λ 4020.

The spectrogram (Plate 84, *A*) represents the absorption of a 0.17 normal solution of uranous chloride in water. Starting with the first strip the depths of cell are 1.2, 2, 4, 8, 16, and 32 mm. For the first three strips the exposures were for 3 minutes to the Nernst glower for all the spectrum; 3 minutes to the ultra-violet, and 1 minute to the spark. The other three strips were exposed to the Nernst glower for 3 minutes. The slit-width was 0.15 mm. and the current in the glower 0.9 ampere. No exposure to the ultra-violet was made for the upper strips, as it was considered that this region would be entirely absorbed. The spectrogram shows, however, that this would not have been the case.

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[1] Phys. Rev., 29, 555 (1909); 30, 279 (1910).

[2] *Ibid.*

Strip 1 shows complete ultra-violet absorption up to about λ 3300. Two absorption bands λλ 4200, 4400 almost merge into each other. Of these the one with shorter wave-length (λ 4270) is considerably stronger than the other (λ 4370). A strong band appears at λ 4980, about 30 Ångström units wide. This is limited by a wide region of general absorption, which widens out very rapidly towards the violet with increasing depth of cell. This is most likely due to the presence of diffuse bands in this region. The diffuse band at λ 5500 widens symmetrically with increasing depth of cell. There are two very strong bands which for 2 mm. depth of cell are situated at λ 6430 to λ 6620 and λ 6720 to λ 6770. This region of absorption is a very characteristic one for uranous chloride in water. Other diffuse bands appear at λ 3910, λ 4030, λ 4600, and λ 6340.

URANOUS AND ALUMINIUM CHLORIDES IN WATER.

Uranyl chloride was reduced in the presence of an aluminium chloride solution of about 2.4 normal concentration. The concentration of uranous chloride was 0.17 normal. Plate 84, *B*, represents the absorption spectrum, the depths of cell being 1.2, 2, 4, 8, 16, and 32 mm.

The resulting spectrum is very much like that of the pure aqueous solution. The ultra-violet absorption is much greater; the absorption extending to about λ 3800. The presence of aluminium brings out several bands in the blue-violet region which we shall continue to designate as the uranyl bands. These bands have the same wave-lengths as the corresponding wave-lengths of the uranyl bands of a solution of uranyl and aluminium chlorides in water.

The band at λ 5000 is much more diffuse than the corresponding band for water. The band at λ 5570 widens symmetrically with increasing depth of cell. Besides these bands there are two bands at λ 6550 to λ 6640 and λ 6750 to λ 6800. The general effect of the aluminium chloride is to bring out the uranyl bands; to increase the ultra-violet absorption; to make the band λ 5000 and others slightly more diffuse, and to cause the uranous bands to shift towards the red, about 20 or 30 Ångström units.

The concentration of uranium in a solution necessary to bring out the uranyl bands either in the uranyl or uranous condition is about the same.

Spectrogram, Plate 98, *A*, shows the effect of the presence of aluminium chloride and hydrochloric acid upon the uranous bands. Strip 1 represents the absorption of a 3 mm. 0.17 normal solution of uranous chloride in water; strip 2 the same to which a 3.04 normal solution of aluminium chloride had been added, so as to make the depth of cell 4 mm.; strip 3 a depth of cell of 6 mm.; strip 4 represents the same as strip 1; strip 5 is the absorption of the solution of strip 4, to which sufficient hydrochloric acid had been added to make a depth of cell of 16 mm. Both aluminium chloride and hydrochloric acid cause the ultra-violet absorption to increase very much. Aluminium chloride has much the same effect as hydrochloric acid, although not so great. It does not change the water-bands λ 6400 and λ 6655 as does hydrochloric acid. Strip 3 gives bands at the following positions: *g*, λ 4140; *f*, λ 4280 (strong); *e*, λ 4400 (*e* and *f* almost merge into each other); *d*, λ 4490; *c*, λ 4620; *b*, λ 4780, λ 4990, λ 5550, λ 6460 to λ 6660, λ 6780.

Two cubic centimeters of a normal aqueous solution of uranyl chloride were added to 8 c.c. of a 3.04 normal aqueous solution of aluminium chloride and to this were added 2 c.c. of hydrochloric acid and zinc, so that the uranyl salt was reduced to the uranous condition. To a 2 mm. depth of solution was added water so as to make the depth of cell 7 mm. The addition of water caused the *b, c, d,* and *e* bands to become very faint and to be shifted to the violet. The band at λ 4980 and especially the bands at λ 5500, λ 6500, and λ 6750 were very considerably shifted. The solution of 7 mm. thickness showed bands at $\lambda\lambda$ 4130, 4210 (narrow), 4285, 4420(?).

URANOUS CHLORIDE IN HYDROCHLORIC ACID AND ACETONE.

A 0.2 normal solution of uranyl chloride in strong hydrochloric acid was reduced by using as little zinc as possible. Plate 70, *A*, shows the absorption spectra of this solution to which acetone has been added. Strip 1 represents the absorption of 5 mm. of the hydrochloric acid solution; strip 2 the same to which 1 mm. of acetone has been added; strip 3, 3.3 mm. acetone, and strip 4, 12 mm. of acetone. The solution was thoroughly mixed in each case.

	Strip 1.	Strip 4.
a	4980 (100 Å. U. wide)	4925(20)
b	4800	4760(20)
c	4620	4590(s) 4535(15)
d	4410	4425(s) 4470(f 20) 4380(f 20)
e	4280	4290(s) 4340(w20) 4240(w20)
f	4140	4160(s) 4200(w20) 4115(w20)
g	4010	4040

In strip 1, *a* consists of a strong broad band. As acetone is added this breaks into two components; the longer wave-length component disappearing as more and more acetone is added. In strip 1 the *d* band has a very diffuse band near it on the long wave-length side. In addition to the uranyl bands there is a broad band at λ 5550; one from λ 6450 to λ 6680 and from λ 6720 to λ 6820. In strip 4 all the broad uranous bands have disappeared and there remain only fine bands from 10 to 20 Ångström units wide. These are located at $\lambda\lambda$ 6780, 6740, 6690, 6625, 6600, 6555, 6490, 6470, 6040, 6000, 5960, 5910, 5220, 5210, and 5195.

URANOUS CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND WATER AND OF METHYL ALCOHOL AND ACETONE.

Plate 89, *A* and *B*, represents the absorption spectra of a constant amount of uranous chloride in mixtures of methyl alcohol and water (*A*); and of mixtures of methyl alcohol and acetone (*B*); the lower strip representing the methyl alcohol solution.

As the amount of water increases the water-band λ 6750 comes out gradually. The methyl alcohol band λ 5050 to λ 4850 is probably double. This narrows on the red side into a band at λ 4850. The methyl alcohol bands λ 4770 and λ 4600 practically disappear, and the band λ 4670 becomes very weak. In their places appear the water-bands λ 4700 and λ 4550.

The *de* band of the methyl alcohol solution λ 4300 to λ 4450 weakens and breaks up, giving the *d* band at λ 4400 and the *e* band at λ 4280. This *e* band is a broadened band otherwise similar in appearance to the band λ 4300 in methyl alcohol, which appears quite narrow. The methyl alcohol bands *f*, λ 4230, and *g*, λ 4120, become the *g* water-band at λ 4160, apparently by coming together.

The most important change produced by adding acetone to a methyl alcohol solution of uranous chloride is to bring in a lot of narrow acetone bands in the region λ 6000 to λ 6500, and the strong absorption band from λ 6500 to λ 6800. There also appears a band at λ 5600.

URANOUS CHLORIDE IN WATER AND ETHYL ALCOHOL.

The addition of ethyl alcohol (spectrogram 96, *A*) to an aqueous solution of uranous chloride causes a very marked change in the absorption spectrum; the water-bands gradually disappearing being replaced by ethyl alcohol bands. This spectrogram shows the decrease of intensity of the water-bands very well. Strip 2 represents a 3.2 mm. depth of uranous chloride in water; 3 the same to which 1.2 mm. of ethyl alcohol has been added; 4 the same as 3 to which 2.2 mm. of ethyl alcohol has been added; 5 equals 4+6 mm. ethyl alcohol, 6 equals 5+10 mm. ethyl alcohol. The upper strips are weak on account of the formation of a precipitate.

URANOUS CHLORIDE IN ACETONE AND WATER.

Plate 85, *A* and *B*, represents the absorption spectra of uranous chloride in mixtures of acetone, *A* representing the more dilute solution of uranous chloride. The lower strip represents the absorption of an almost pure acetone solution, the other strips representing the absorption of the same solution to which greater and greater amounts of water are added.

This spectrogram shows that several of the uranyl bands are characteristic of acetone and aqueous solutions. The absorption of an acetone solution in the region λ 6500 is much less and consists of but a single band. The aqueous solution, on the other hand, has a very characteristic band at λ 6750. The band at λ 5550 of the acetone solution is shifted towards the violet as water is added.

As the percentage of acetone is decreased the acetone bands *a*, λ 4920, *b*, λ 4750, and *c*, λ 4590, gradually disappear, while the water-bands *a*, λ 4980, *b*, λ 4700, and *c*, λ 4570, gradually increase in intensity. No shift is to be noticed.

The other uranyl bands appear but slightly changed; the positions and intensities of the acetone and water-bands being about the same. For the acetone solution they are *de*, λ 4430, *f*, λ 4290, *g*, λλ 4160, 4130, *h*, λλ 4040, 4010, and *i*, λ 3910. For the aqueous solution they are *de*, λ 4450 (weak), *f*, λ 4290, *g*, λ 4150, and *h*, λ 4010.

URANOUS CHLORIDE IN METHYL AND ETHYL ALCOHOLS.

In Plate 88, *A* represents the absorption of a dilute solution of uranous chloride in ethyl alcohol, and *B* in methyl alcohol. The depths of cell were 3, 6, 12, 24, and 35 mm., slit-width 0.15 mm., exposure to Nernst glower

1.5 minutes to the whole spectrum, 2 minutes to the ultra-violet of the Nernst glower, and 1 minute to the spark.

The absorption for the two solvents is very much the same; the bands being much alike in intensity and position. The methyl alcohol bands are of slightly shorter wave-length.

Ethyl alcohol solution: λ 4290 (narrow), λ 4710, λ 4950 to λ 5050, λ 5280 (weak), and λ 6200 to λ 6300.

Methyl alcohol solution: λ 4000, λ 4130, λ 4250, λ 4290 (narrow), λ 4700, λ 5020, λ 5260, and λ 6150 to λ 6300.

A solution of the uranous chloride in methyl alcohol stood for almost a year. The absorption of this solution was quite different from that described above. This was probably due to the much larger amount of hydrochloric acid and zinc chloride in the old solution; as small amounts of hydrochloric acid as possible having been used in the solution described above. The position of the bands of the "old" solution were: λ 3910 (double), λ 4020 (double), λ 4130 (double), λ 4590, λ 4750, λ 4710, λ 5000, λ 5550, and λ 6500 to λ 6800.

URANOUS CHLORIDE IN GLYCEROL.

In making a glycerol solution of uranous chloride a strong solution of uranous chloride is made in some other solvent. It is then mixed with glycerol and warmed. The warming is continued until as much of the other solvent is evaporated as possible. Spectrograms are then made of different depths of this solution, and of mixtures of glycerol with some other solvent. Plate 87, *C*, represents the absorption spectra of a glycerol solution of uranous chloride of different depths; starting with the lowest strip the depths being 3, 4, 6, 9, 12, 18, and 24 mm. As the reduction was not complete it is impossible to know the concentration of the uranous chloride, although this could be found approximately. The spectrogram shows the uranyl bands and the uranyl blue-violet band. Knowing the depth of layer and having made the spectrogram it is possible to know quite accurately the amount of uranyl chloride in the solution. The remainder of the uranium chloride is probably in the uranous condition.

The uranyl bands, *i*, λ 3800, *h*, λ 3930, and *g*, λ 4050, are very weak and about 60 Ångström units broad. The band *f*, λ 4170, is fairly strong, as is also *e*, λ 4310; *d* is double, consisting of a wide diffuse band at λ 4440 and a narrower diffuse band at λ 4530; *c*, λ 4680, and *b*, λ 4840, are both very strong, and about 80 Ångström units wide; *a*, λ 4980, is very narrow and has a very weak band at about λ 5060. The weak band at λ 5060 is barely visible in the original negative. For the greater depths of cell, bands several hundred Ångström units wide and extremely diffuse appear at about λ 5300, λ 5600, and λ 6300. These will be more fully discussed when uranous chloride in mixtures of glycerol and other solvents is described.

URANOUS CHLORIDE IN MIXTURES OF GLYCEROL AND WATER.

Spectrogram, Plate 86, *A*, represents the absorption of a solution of uranous chloride in glycerol to which water is added. Strip 1 represents the absorption of a 6 mm. solution of uranous chloride in glycerol; the other strip showing the effect of adding water; the amount of water added being very small for the first few strips.

For strip 1 the absorption consists largely of the bands *a*, λ5000 (very broad and probably double), *b*, λ4840; *c*, λ4680; *d*, λ4530, λ4440 (latter component very strong); *e*, λ4310; *f*, λ4170; and *g*, λ4050.

The addition of water causes the absorption in the region λ 6250 to increase. There are also broad absorption bands at λ 5000 and λ 5250, which are very diffuse and are somewhat stronger for the aqueous solution. The *b* glycerol band disappears entirely. The *c* glycerol band breaks up into two, and as the amount of water increases one of these moves rapidly towards the violet. The stronger component remains practically stationary. In strip 7 their wave-lengths are λ 4565 (weak) and λ 4690 (strong and about 30 Ångström units wide). The faint component of *d* disappears and there is left a very diffuse band at about λ 4420. The *e* band is double with components at λ 4250 and λ 4290. About these components there is a very considerable amount of general absorption. The *f* band is at λ 4150.

URANOUS CHLORIDE IN MIXTURES OF GLYCEROL AND METHYL ALCOHOL, GLYCEROL AND ETHYL ALCOHOL, AND GLYCEROL AND ACETONE.

The addition of methyl and ethyl alcohols causes very little change in the bands. Any large addition of acetone causes a precipitate to be formed.

	Glycerol solution.	Methyl alcohol.	Ethyl alcohol.	Acetone.
a	5000	5000 (broad)	5000	5000(weak)
b	4840	4815	4820	4840
c	4680	4650	4660	4680
d	4530 4440	4450 (very broad)	4460	4530 4450 } weak
e	4310	4280	4280	4310
f	4170	4140	4140	4180
g	4050	4030	4030	4055

URANOUS CHLORIDE IN ACETONE, IN METHYL ALCOHOL, AND IN GLYCEROL.

Plate 95, *A*, represents the absorption spectra of a solution of uranous chloride in acetone, the depth of cell being 1.2, 2, 3, 5, 8, and 11.5 mm. The slit was 0.10 mm. in width, current in Nernst glower 0.94 ampere, exposure 1.5 minutes to glower and 3 minutes to the spark. The bands are faint and diffuse. By the addition of hydrochloric acid they are made very much stronger, although the wave-length of the bands is not changed.

Plate 95, *B*, represents the absorption spectra of uranous chloride in methyl alcohol; the depths of cell being 2, 4, 6, 8, and 12 mm. These solutions had been made about six months before being used. Bands appear at λ 6650, λ 6200, λ 5600, λ 5250, λ 4900 to λ 5070, λ 4780, λ 4665, λ 4600, λ 4230, and λ 4110. The absorption is very strong throughout the region λ 4200, and is so general that there is hardly any banded appearance.

Plate 95, *C*, represents the absorption of a solution of uranous chloride in glycerol (the glycerol also contained strontium chloride). The depths of cell were 2, 4, 6, 8, 12, and 24 mm. The absorption spectra show the uranyl bands, and the large uranyl blue-violet band. Besides these there is a diffuse band at λ 5300 and a band at λ 6200 which broadens rapidly as the depth of cell is increased. The uranyl bands are located as follows: *a*, λ 4980; *b*, λ 4840; *c*, λ 4680; *d*, λ 4445 (weak band at λ 4530); *e*, λ 4300, to *f*, λ 4170.

URANOUS CHLORIDE IN METHYL ALCOHOL AND ETHER.

Two photographs were made, one of uranous chloride in methyl alcohol (next to the spark spectrum), and one of uranous chloride in a mixture of about 60 per cent methyl alcohol and 40 per cent ether. Further addition of ether caused a precipitate to be formed so that the absorption spectra could not be obtained.

The methyl alcohol solution showed complete ultra-violet absorption to λ 3700. The region λ 4300 showed considerable general absorption due to the blue-violet band. The following uranyl bands appear: *i*, at λ 3880, *h*, at λ 4000, *g*, composed of two bands one at λ 4110 and a narrow band about 10 Ångström units wide at λ 4135, *f*, of two bands, λ 4240 and λ 4285, the latter being quite narrow, *d* and *e* form one very broad band at about λ 4400, *c* at λ 4610, and *b* at λ 4780. Two bands, λ 4930 (*a*) and λ 5050 are almost merged into each other.

The addition of ether caused the absorption to increase; the ultra-violet absorption extending to λ 3800 and the absorption from λ 4100 to λ 4450 being almost complete. The uranyl bands are slightly shifted towards the red. Their general character remains the same. The wave-lengths are approximately, *i*, λ 3890, *h*, λ 4010, *g*, λ 4140, *f*, λ 4260, *de*, λ 4440, *c*, λ 4630, *b*, λ 4790, *a*, λ 4960, and a band at about λ 5050.

The effect of ether is to cause the bands to shift slightly to the red and to increase the amount of absorption.

EFFECT OF THE PRESENCE OF ACIDS ON THE URANOUS BANDS.

A spectrogram was made of a 3 mm. solution of 0.17 normal uranous chloride in water (strip 1). To this was added very strong hydrochloric acid until the depth of cell was 6 mm. (strip 2), and finally until it was 12.5 mm. (strip 3), and 24 mm. (strip 4).

The effect of hydrochloric acid is very marked. In general it shifts the uranyl and uranous bands to the red. It causes the uranyl bands to appear much stronger. In an aqueous solution the λ 6400 band is very broad, and the λ 6655 band comparatively narrow. Hydrochloric acid reverses the appearance of these two bands; shifting both towards the red at the same time. The following wave-lengths give the effect of hydrochloric acid:

	Strip 1.	Strip 2.		Strip 1.	Strip 2.
b	....	4800	*b*	4875	5000
c	....	4640	*c*	5520	5620
d	....	4490 (weak)	*d*	6340 (weak)	....
e	4380 (weak)	4420 (strong)	*e*	6430-6600	6500-6570
f	4280 (strong)	4280 (strong)	*f*	6755	6700-6850
g	4130	4150	*g*		

An aqueous solution of uranous chloride in concentrated hydrochloric acid gave the uranyl bands very distinctly. The uranium salt was reduced in this case in the presence of hydrochloric acid. The spectrum is almost identical with that of uranous chloride when hydrochloric acid is added after the reduction has taken place.

The addition of about 20 per cent strong sulphuric acid to an aqueous solution of uranous and aluminium chlorides has a very marked effect upon the bands. The general effect is to shift the bands towards the violet. For the uranous chloride solution containing aluminium there is a band about 50 Ångström units wide at λ 6770 and a band from λ 6460 to λ 6640. These are the water-bands. When sulphuric acid is added there is a wide band from λ 6600 to λ 6760, a narrow band at λ 6480, and a wide band running from λ 6200 to λ 6400. Sulphuric acid reverses the breadth of the two red water-bands.

The water-band at λ 5500 is shifted to the violet and doubled by the addition of H_2SO_4, the resulting bands being λ 5500 (strong) and λ 5400. The uranyl bands are all shifted to the violet as follows: *a*, λ 4990 to λ 4890; *b*, λ 4780 to λ 4750; *c*, λ 4620 to λ 4560; *d*, λ 4400 (λ 4490 weak) to λ 4360; *e*, λ 4280 to λ 4220; *f*, λ 4140 to λ 4080.

URANOUS CHLORIDE IN WATER AND METHYL ALCOHOL; WATER AND ACETIC ACID; WATER AND NITRIC ACID; AND IN WATER AND SULPHURIC ACID.

Strip 1, Plate 98, *B*, is a 4 mm. depth of layer of a 0.17 normal aqueous solution of uranous chloride; strip 2 is the one to which the depth of layer has been increased to 6.3 mm. by adding methyl alcohol; strip 3, addition of methyl alcohol until depth of layer is 7.5 mm.; strip 4 is a 4 mm. 0.17 normal aqueous solution of uranous chloride; strip 5 is 4 to which acetic acid has been added to make the depth of layer 28 mm.; strip 6 is a 4 mm. 0.17 normal aqueous solution of uranous chloride + 2 mm. of strong nitric acid; strip 7 is a 4 mm. 0.17 normal aqueous solution of uranous chloride to which 19 mm. of sulphuric acid had been added:

	Strip 1.	Methyl Alcohol. Strip 3.	Acetic Acid. Strip 5.	HNO_3. Strip 6.	H_2SO_4. Strip 7.
b	.....	.....	4785	.....	4750 (very diffuse).
c	.....	.....	4620	.....	4550 (very diffuse).
d	.....	.....	4450	.....	4400
e	4380	.....	4280–4245	4330 *e* ?	4340
f	4280	4255	4130 *f* ?	4240 *f* ?	4220 (double narrow component on violet side).
g	4130	.....	.....	4120 *g* ?	4100
	4875	4670 (characteristic)	.....	4800 (very diffuse)	4900 (wide and strong).
	5520	5000 (very diffuse)	4900–5000	5450 (very diffuse)	5390–5490 (almost join).
	6340	5250 (very diffuse) 6200 (very diffuse)	5500 (very diffuse)	6500 (50 Å. U. wide)	6250–6380
			.....	6670–6760	6490 (30 Å. U. wide).
	6420–6620	.....	6450–6800	.....	6610–6760 (quite well defined).
	6755				

Plate 90, *A*, strip 1, represents the absorption of a 1.8 mm. solution of uranous chloride in acetone (a different solution from that previously described and one which instead of having been freshly prepared had been made about 2 weeks before using); strip 2 represents the absorption of the same solution to which 0.5 mm. hydrochloric acid had been added; strip 3 the same as 1 to which 1.2 mm. of hydrochloric acid had been added (in this case a small amount of a brown precipitate was formed causing the absorption to be greatly increased); strip 4 represents an ether solution (ether was added to the acetone solution of uranous chloride, a deep green precipitate was formed, and the ether became yellow) of probably uranyl chloride; strip 5 represents the absorption of an acetone solution of uranous chloride, freshly prepared, 2 mm. in depth, strip 6 the same 5 mm. in depth, and strip 7, 14 mm. in depth.

The freshly prepared uranous chloride (in acetone) solution shows the uranous bands very faintly. The addition of hydrochloric acid is seen to bring out the bands very well. In addition to the bands already described faint bands (strip 2) appear at λ 6090, λ 6340, λ 6365, and λ 6390. The ether bands occur as follows: *a*, λ 4930; *b*, λ 4760 (a faint component at λ 4800); *c*, λ 4600; *d*, λ 4440; *e*, λ 4290; *f*, λ 4155; *g*, λ 4030. The relative shifts of the ether bands relative to the bands of the solution of uranous chloride in hydrochloric acid are very noticeable when the spectrograms are made to overlap. With reference to these bands the ether bands *d*, *e*, *f*, and *g* are shifted to the red and the *a* and *b* bands to the violet.

URANOUS CHLORIDE TO WHICH ACETIC ACID IS ADDED.

Plate 94, *B*, represents a slightly acid solution of uranous chloride in water to which is added glacial acetic acid until there is five times as much glacial acetic acid present as there was of the original solution. The addition of acetic acid causes a marked change in the absorption. *a*, λ 4980, doubles into the bands λ 5020 and λ 4930; *b* and *c* double without being changed very markedly; *d*, λ 4400, is slightly shifted to λ 4420; *e*, λ 4280 to λ 4300; *f*, λ 4140 to λ 4160; and *g*, λ 4010 to λ 4030; λ 5560 is shifted to λ 5590; λ 6450 to λ 6650 to λ 6500; and instead of the band at λ 6770 there are two bands λ 6650 and λ 6800.

URANOUS BROMIDE.

Plate 92, *A*, represents the absorption of an 0.8 mm. depth of 0.5 normal uranous bromide in water to which more and more water has been added. The depths of cell are 0.8 mm., 2.8, 12.5, 22, and 35 mm.

The ultra-violet absorption is but slightly changed by the addition of water. The other uranous bands are narrower the greater the dilution of the uranous bromide. For the upper strip the positions of the bands are λ 4280, λ 4370 (these bands form practically a single band), λ 4850 (very diffuse), λ 4970 (these bands merge into each other), λ 5400 to λ 5600, λ 6200 to λ 6650 and λ 6750.

URANYL AND URANOUS ACETATES.

The action of free acetic acid upon the uranyl absorption bands of an aqueous solution of uranyl acetate is quite small. The bands are made quite narrow and weak. One spectrogram gave *b*, λ 4730; *c*, λ 4610; *d*, λ 4470; *e*, λ 4330; and *f*, λ 4210. This is very similar to the absorption spectra of the anhydrous salt. Uranous acetate in water (Plate 96, *B*) gives a lot of weak diffuse bands. The bands are located at *c*, λ 4600; *d*, λ 4460; *e*, 4330; *f*, λ 4200; and *g*, λ 4090. Besides these are broad bands at λλ 5050, 5600, 6700, and 6850.

ABSORPTION SPECTRUM OF DRY URANOUS ACETATE.

The green precipitate that is formed when a solution of uranous acetate in methyl alcohol stands for several hours was illuminated by light from the Nernst glower; the illuminated salt being over the slit of the spectroscope. The green salt changed to a dark color probably due to oxidation.

The absorption spectra showed weak diffuse bands at λλ 4240, 4350, 4500, 4650, and a wide band running from λ 4900 to λ 5200. If these bands are to be identified as the *f* (λ 4240), *e* (λ 4350), *d* (λ 4500) and the *c* (λ 4650) bands; and their relative intensities are about the same as that of the bands of uranous acetate in methyl alcohol; then the bands are slightly shifted towards the red, this shift being about 50 Ångström units.

URANOUS ACETATE IN METHYL ALCOHOL AND ACETIC ACID.

To a solution of uranyl acetate in methyl alcohol was added glacial acetic acid and some metallic zinc. The solution becomes green in color after standing a few minutes. In an hour or more a greenish precipitate is formed, and after standing several hours the solution shows only the uranyl bands. The plate represents the absorption spectra of the green uranous acetate. The only variation here is the depth of cell. For the three strips nearest the top the depth of cell was the same.

Starting in the ultra-violet the spectrogram shows a general absorption which extends into the blue for the greater depth of layer. No indication of the blue-violet uranyl band is to be noticed. Several fine bands appear in the blue-violet region. As these coincide very closely in position with the uranyl acetate bands they will be so considered. Of these the *a*, *b*, *c*, *d*, *e*, *f*, and *g* bands appear. The *g* band (λ 4070) is very faint. The *f* band (λ 4200) is stronger and is about 30 Ångström units wide. The *c*, *d*, *e*, and *f* bands appear quite strong; the *e* band being the strongest. It appears to be complex, being composed of a fuzzy band at λ 4285 about 10 Ångström units wide; a fine sharp band at λ 4310 about 3 Ångström units wide, and a band extending roughly from $\left\{\begin{smallmatrix}\lambda\ 4315\\ \lambda\ 4316\end{smallmatrix}\right\}$ to λ 4340. The *d* and *c* bands (λλ 4470 and 4610) are about 30 Ångström units wide and of about equal intensity. The *a* and *b* bands are very weak (λλ 4910, 4740) and only appear on the original negative.

The *a* band with two other very diffuse bands λλ 5000, 5100 form the wide absorption band in this region and practically merge into each other. A similar band extends from λ 5550 to λ 5650. In the red there are quite a number of fine bands very similar to the uranyl group in the blue and violet. These are very faint; the widest and strongest appearing at λ 6450; this band being about 40 Ångström units wide. The other bands are about 20 Ångström units wide and are located approximately at λλ 6600, 6700, 6800, 6870, and 6920.

URANOUS ACETATE IN GLYCEROL.

Uranous acetate was obtained as already described. Some of the solution in methyl alcohol and acetic acid was mixed with glycerol and warmed so as to drive off as much alcohol and acid as possible. The solution was filtered hot. The precipitate was green, the filtrate yellow; indicating that the uranium in the glycerol was mostly in the uranyl condition.

The absorption spectra showed several of the uranyl bands. These bands are not nearly so intense as the bands of uranous acetate in methyl alcohol and acetic acid. The *f* band λ 4220 appears to be double. The *e* band consists of a band about 15 Ångström units wide at λ 4295, a band at λ 4340, and one at λ 4390; the *d* band of two bands λ 4480 and λ 4530; and the *c* band of λ 4630 and λ 4680, the latter being the weaker of the two bands.

EFFECT OF TEMPERATURE ON THE ABSORPTION SPECTRA OF URANOUS CHLORIDE.

A spectrogram was made to show the effect of change in temperature on the absorption spectrum of an aqueous solution of uranous chloride. To a normal solution of uranyl chloride in water was added a small amount of zinc and hydrochloric acid. The hydrogen reduced the uranyl chloride to uranous chloride—a deep green solution which seemed quite stable. The solution was then placed in the trough of the temperature apparatus and an exposure made in the usual manner. The thickness of layer was 1 mm. The exposures were 50 minutes to the Nernst glower and 4 minutes to the spark. The current through the glower was 0.8 ampere and the slit-width 0.20 mm. Starting with the strip nearest the comparison scale the temperatures were 8°, 17°, 33°, 48°, 62°, and 73°. An exposure was made at 80° and will be described with the other exposures although it is not on the spectrogram as printed.

At 8° a slight mist formed on the prisms on account of their low temperature and the humidity of the air. For this reason the strip is very much underexposed and the bands apparently seem wider than at the higher temperatures. At this temperature there is complete absorption to λ 3650. A blue-violet absorption runs from λ 4050 to λ 4450. Following this are three strong bands of about equal intensity and each about 100 Ångström units wide. These bands are located approximately at λλ 4590, 4760, and 4970. Then comes a band at about λ 5510, a wide band from λ 6400 to λ 6630, and a rather narrow band at λ 6740.

At 73° the spectrum is very similar to that at 8°. The amount of absorption has, however, increased quite considerably and all the bands have widened. The ultra-violet band has widened to λ 3800 and the blue-violet band practically runs from λ 4050 to λ 5000; although there is some transmission between the bands λλ 4610, 4770, and 4980. It will also be noticed that these bands have been slightly shifted towards the red. This shift is quite small, and on account of the haziness of the bands is hard to measure definitely. None of the other bands appear to be shifted. The band at λ 5500 has become about twice as wide as it was at the lower temperatures, and the two red bands have practically merged, running from λ 6350 to λ 6800.

Between 73° and 80° the absorption has increased very markedly. The whole spectrum is practically absorbed up to λ 5050. The band in the green runs from λ 5450 to λ 5600, and the band in the red has also widened very greatly, extending from λ 6200 to λ 6800.

The Wave-Lengths of the Uranous and Uranyl Bands Under Varying Conditions in Aqueous Solutions.

	Uranyl nitrate.	Uranyl chloride.	Uranous bromide.	Uranyl nitrate in HNO_3.	Uranous chloride.	Uranyl acetate.	Uranous acetate.	Uranyl bromide.	Uranyl acetate.	Uranyl sulphate.
a	4870	4920	4970 4880	4850	4980	4910	....	4880	4910	4900
b	4705	4740	4740	4670	4790 *w*	4740	....	4720	4740	4740
c	4550	4560	4600	4520	4550 *w*	4600	4600	4560	4595	4580
d	....	4460	....	4380	4420 *w*	4460	4460	4450	4455	4460
e	4310	4315	....	4240	4305 4270	4310	4330	4280	4310	4330
f	4155	4170	....	4140	4150	4160	4200	4160	4160	4200
g	4030	4025	....	4050	4020	4070	4090	....	4070	4070
h	3905	....	....	3920	3910	3970	....	....	3970	3970
i	3815	....	....	3810	....	3830	....	....	3830	3850
j	3710	....	....	3750	....	....	....	....	....	3740
k	3605	....	....	3670	....	....	....	....	....	3630
l	3515	....	....	3590	....	....	....	....	....	3530
m			6740	3520	5500	....	5050			
			6480	....	6500	....	5600			
			5500	....	6750	....	6700			
					6340	....	6850			

Alcoholic Solutions of Uranium Salts.

Uranous chloride in methyl alcohol gives bands at λλ 6650, 6250, 5600, 5260, 4900–5070, 4780, 4665, 4600, 4230, 4410.

Uranous bromide in methyl alcohol gives bands at λλ 6650, 6200, 5650–5500, 5250, 4950–5100, 4680S, 4450–4300, 4150.

	Uranous chloride in methyl alcohol.	Uranyl nitrate in methyl alcohol.	Uranous acetate in methyl alcohol.	Uranyl nitrate in ethyl alcohol.	Uranous chloride in ethyl alcohol.	Uranyl acetate in methyl alcohol.	Uranous bromide in methyl alcohol.	Uranyl chloride in methyl alcohol.	Uranous chloride in methyl alcohol.	Uranyl chloride in ethyl alcohol.	Uranous chloride in ethyl alcohol.
	5050	....	....	5000	5050 to	4880	5070	....	....	....	....
a	4930	4930	4910w	....	4950	4900	4900	4930	5000	4900	5000
b	4780	4760	4740w	4800	4710	4720	4780	4760	4815	4750	4820
c	4610	4610	4610	4630	....	4590	4665	4610	. 4650 *b*	4580	4665
d *e*	4400 *b*[1]	4455	4470	4475	....	4450	....	4465	4450	4400	4460
f	4285	4325	4330	4325	....	4320	....	4345			
g	4135 4110	4190	4310 4285	4180	4290u	4190	4230	4220	4280	4250	4280
h	4000	4070	4200	4080	....	4070	4110	4090	4140	4100	4140
i	....	3965	4070	3970	....	3980	....	3980	4030	3980	4030
j	....	3855	....	3875	....	....	....	3860 3760	....	3860	
	5260	....	....	....	5280						
	6250	....	....	....	6250						

[1] *b* is broad.

Glycerol Solutions.

	Uranous acetate in glycerol.	Uranous bromide in glycerol.	Uranyl chloride in glycerol.	Uranyl chloride in glycerol.	Uranyl nitrate in glycerol.	Uranous sulphate in glycerol.	Uranous chloride in glycerol.	Uranous chloride in glycerol.
a	....	....	5060 *w*	5050	5040 5020	....	....	....
b	4680 4630 *w*[1]	....	4980 *w* 4840*s*80[2]	4900	4910 4750	4780 +H_2SO_4	5000 4790	5000 4840
c	4530 4480	4700?	4680*s*80	4720	....	4640	....	4680
d	4390 4340 4295	4550*w*? 4430*w*	4530 *n.d.*[3] 4440 *w*	4540 4400	....	4480	4550 4420	4530 *w* 4450
e	4220	....	4300	4260	4350	4365	4300	4310
f	....	4200?	4170	4140	4220	4250	4170	4260 *w*.10
g	....	....	4050 *w*	4025	4100	4120	4050	4170
h	....	....	3930 *w*	3920	3970	4010	....	....
i	....	....	3800 *w*	....	....	3900	....	....
j	....	....	....	....	....	....	....	....
k	....	....	....	....	....	3750	....	....
l	....	....	....	....	....	3650	....	....

[1] *w* means weak. [2] *s*=strong, 80=Å. U. [3] *n. d.*=narrow and diffuse.

Uranyl Salts in the Presence of Free Acid.

	Uranous chloride in water.	Uranous chloride with hydrochloric acid.	Uranyl acetate in acetone with acetic acid.	Uranyl acetate in water.	Uranyl acetate with acetic acid.	Uranous acetate in water.
a	4980	5000	......	4910	....	....
b	4790	4800	4620 ?	4740	4730	....
c	4550	4630	4460 ?	4595	4610	4600
d	4420	4430	4330 ?	4455	4470	4460
e	4305 4270	4270	4220 ?	4310	4330	4330
f	4150	4140	......	4160	4210	4200
g	4020	4020	......	4070	....	4030
h	3910	....	......	3970	....	....
				3830		
	6770					
	6550					
	5620					

Effect of the Presence of Foreign Salts.

	Uranyl chloride in water.	Uranyl chloride + $AlCl_3$	Uranyl chloride + $ZnCl_2$	Uranous chloride +$AlCl_3$	Uranous chloride + H_2SO_4
a	4920	4950	4930	4990	4890
b	4740	4790	4770	4780	4750
c	4560	4620	4600	4620	4560
d	4460	4480 to 4420	4400	4490 4400	4360
e	4315	....	4245	4280	4220
f	4170	4270	4115	4140	4080
g	4030	4135	....	....	....
h	....	4010	....	....	....
i	....	....	....	....	....

Effect of Free Acid.

	Uranyl nitrate in water.	Uranyl nitrate to which H_2SO_4 is added.	Uranyl sulphate in water.	Dry uranyl nitrate in HNO_3.	Uranyl sulphate in H_2SO_4.	Uranyl nitrate in HNO_3.	Uranyl chloride in water.	Uranyl chloride + HCl.
a	4870	4925	4900	4850	4930	4790	4920	4950
b	4705	4750	4740	4670	4750	4670	4740	4800
c	4550	[1] 4560	[1] 4580	4520	[1]4560	4510	4560	4635
d	....	4380	4460	4380	4380	4370	4460	4480
e	4310	4240	4330	4240	4240	4230	4315	4420
f	4155	4100	4200	4140	4100	4125	4170	4280
g	4030	....	4070	4050	....	4000	4025	4050
h	3905	3980	3970	3920	3980	3900	....	4015
i	3815	3870	3850	3810	3870	3790		
j	3710	3770	3740	3750	3770	3670		
k	3605	3660	3630	3670	3660	3570		
l	3515	3560	3530	3590	3560			
				3520				

[1] Double.

Any small differences in the wave-lengths of the absorption bands of uranous solutions under different conditions are probably due to the presence of varying amounts of zinc used in reducing the uranyl to the uranous condition.

CHAPTER XII.

GENERAL DISCUSSION OF RESULTS.

Previous investigators have in many instances spoken of the absorption of light by molecules, ions, or aggregates of these. The present theory of spectroscopy is, however, more and more inclined to consider the negative electron as the chief absorber of light in the visible and ultra-violet portions of the spectrum. Whether the absorbing electron is the same as the electron found in vacuum discharge tubes, or emitted by radioactive elements, is at present a very much discussed subject. It seems to be quite certain that the masses of many of the absorbers are not of molecular magnitude. It is equally certain, as experiments show and as theory indicates, that the various coefficients which define the equations of motion of the absorber are *functions of the conditions under which the absorbers exist.* If the absorbers are electrons we may think of them as being within or in close proximity to the atom. Such absorbers would be expected to have their period, coefficient of damping, and other coefficients greatly modified by the formation of aggregates, solvates, etc., and such seems to be the case. According to the present theory of the conductivity of solutions it would be expected that if the absorbers existed in or about the atom, their properties would be very greatly affected by the given atom existing in an ionic or in a condition as part of a molecule. Consequently, at great dilutions, it would be expected that the absorption of a colored solution of a salt would be entirely independent of the salt when the anion was the carrier of the absorbers. In the absorption spectra of solutions there are but few examples where the absorption spectra of different salts with the same cation are very different from each other. There is one important exception in the case of aqueous solutions of the uranyl salts. The uranyl nitrate bands are all of shorter wave-lengths than the bands of the other uranyl salts. The absorption spectra of these salts have been photographed by us over quite wide ranges in concentration, and no evidence has been obtained that indicates any dependency of the wave-lengths of the uranyl bands on the concentration.

Although more and more spectroscopic phenomena are being explained by means of the electron theory, yet there is a general tendency to consider that only the electrons in a few atoms are in a condition to absorb or emit light at any moment. What the nature of these conditions is, is at present not well known, but it seems probable that they are *exceptional states* in some cases at least. For instance, only a few of the sodium atoms take part in the absorption of the *D* lines at any particular time, and the same is probably true of neodymium and erbium salts in solution or in the solid state. It is supposed by some physicists that absorption or emission may take place during ionization, as, for example, when an electron leaves or returns to an ion. Upon a basis such as this is laid the theories of dynamic isomerism, isorepesis, and Stark's theory of the spectrum of canal rays and of fluorescence. On such a theory as this it may be supposed that in solutions the absorption took place in those molecules that are undergoing dissociation, or in those ions that are combining to form molecules. In the case of the uranyl nitrate bands it was pointed out that the combined action of water and the NO_3 group had a hypsochromous effect upon the wave-lengths of these bands. That it is due to the combined action of the water and the NO_3 group is shown by the fact that in other solvents the NO_3 group does not have this hypsochromous effect; while in water it is only the nitrate bands that have the smaller wave-lengths. According to the theory of dynamic ionization the absorption of light could take place while the NO_3 groups were near the UO_2 group, so that the periodicity of the absorbed light would be affected. According to this theory, however, the number of ionizations through which a molecule would pass would probably be a function of the concentration; and thus the intensity of the absorption bands should be a function of the concentration. But for uranyl nitrate Beer's law holds at least approximately, whereas considerable variations would be expected from the above theory. If the absorption takes place during periods of ionization, and the intensity of the absorption depends only on the number of these ionizations, then the fact that Beer's law holds shows that the number of these ionization phenomena is independent of the concentration. The fact that the absorption spectrum of uranyl nitrate crystals is very similar to solutions indicates that the uranyl groups that take part in absorption are about as closely united with water and the NO_3 group in solution as they are in the solid.

It may, however, be said in general, *that the anions of the various colored salts*—and in practically all cases it is the anion that exhibits banded absorption—*play a much less important rôle in modifying the spectra than the solvent.* Different salts of the same anion in the same solvent usually have the same absorption spectra. On the other hand, the absorption spectra of the powdered salts themselves may be very different. This fact shows that *the solvent plays a most important part in the absorption,* and it *seems highly probable that in a large number of cases there is an "atmosphere" of the solvent molecules about the colored absorber. In a word, there is solvation.* However, in the case of the nitric oxide[1] spectrum it seems possible to have the gas existing in solution and at the same time having its absorption spectra unaffected. The nitric oxide spectrum only occurs under very special conditions, and has not thus far been obtained for solutions of the gas, but only when some acid is added to nitric acid or a nitrate. It would seem probable that in this case no chemical reaction or "atmosphere" of the solvent existed.

Whereas the absorption of different salts of the same colored anion is in general very similar, on the other hand, the *absorption spectra of the same salt in different solvents are often very different indeed.* Formerly this effect of the solvent was thought to be due to a difference in the value of the dielectric constant, but Jones and Anderson have pointed out that the most probable cause is the *formation of solvates, or more or less stable com-*

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[1] Phys. Rev., **30, 279 (1910).**

pounds of the salt and solvent. The reason *for this conclusion is that in mixtures of two solvents, each set of solvent bands appears; the intensity of any solvent band being a function of the relative amounts of the solvents present.* That these compounds or solvates have a definite composition seems to be indicated by the fact that for most of the neodymium, uranyl, and uranous salts there appears only a single set of "solvent" bands for each solvent; and in mixtures of these solvents in most cases but two sets of bands are necessary to explain the results. The persistence of solvent bands varies quite widely for the different solvents, and appears to be greatest for water and glycerol and less for the alcohols. This persistence of any one solvent band seems to be the same for quite widely different salts. There are, however, some cases where it may be possible that intermediate solvates are formed. Neodymium chloride dissolved in mixtures of water and glycerol seems to indicate that the "water" band λ 4274 gradually shifts to the "glycerol" bands.

Probably no salts show more characteristic bands than some of the uranous salts in the various solvents: water, the alcohols, acetone, and *glycerol.* It seems probable that the absorbers are the same for the corresponding bands of any two "solvent" spectra. An important fact indicating this is given by Becquerel, who found the Zeeman effect to be the same when different solvents of the same salt were used. It is generally conceded that at higher temperatures solvates are broken up. At present, work is being done on solutions containing mixtures of two solvents in such proportion as to give both sets of solvent bands. As the critical temperature of one solvent is approached, according to the foregoing theory, the bands of that particular solvent should disappear. In many cases the two sets of solvent bands differ not only in wave-lengths but also in intensity, and in the number of components. Of all the bands of the neodymium absorption spectra, the "water" band λ 4274 is one of the strongest, and one that is freest from neighboring bands. Yet, in different solvents this band may become a doublet, a triplet, or may even apparently break up into a whole series of bands. It is quite certain that when the mechanism of these changes is known, our knowledge of chemical compounds will be increased very greatly, and it is very important that gradual changes of solvent or salt may be made at low temperatures where the bands are much sharper, and work is now in progress on this problem.

In some cases it is possible to break up the absorption bands by chemical methods into very fine bands. A very striking example is the case of uranyl and uranous salts in acetone solutions. The uranyl salt in acetone gives six bands in the region λ 5000 that are characteristic of acetone solutions. By the addition of hydrochloric acid to an acetone solution the uranyl bands are broken into fine components. Several of the uranyl bands become triplets and some doublets. But the most marked example is the addition of hydrochloric acid to an acetone solution of uranous chloride. Several very broad uranous bands are broken up into a number of very fine and quite intense bands.

One very interesting result has come to light from the examination of the effect of free nitric acid on the absorption spectra of uranyl nitrate;

of sulphuric acid on the sulphate; acetic acid on the acetate; or hydrochloric acid, calcium, or aluminium chloride on the chloride. In general the *presence of these foreign reagents causes the uranyl bands to become more intense and, in most cases, narrower. The action of all the above reagents except nitric acid is to cause the uranyl bands to be shifted towards the red.* Nitric acid, however, causes large shifts towards the violet. The above reagents have a similar effect on the corresponding uranous bands.

The explanation of the above effects seems possible by supposing that aggregates are formed. In the case of neodymium salts the effect of the above reagents is very small, and nitric acid, instead of causing the neodymium nitrate bands to become narrower, stronger, and to be shifted towards the violet, simply causes the bands to become much more diffuse. The other reagents cause the neodymium bands to become diffuse, weaker, and to broaden somewhat towards the red.

In addition to trying the effect of acids upon uranium salts of the same acid, *spectrum photographs were made of the effect produced by adding acids to different uranyl, uranous,* and *neodymium salts.* Uranyl nitrate was treated with sulphuric, hydrochloric, and acetic acids; uranyl and uranous acetates with various acids; various uranous salts and neodymium acetate with nitric acid. These salts and acids were selected, since they showed the greatest spectroscopic changes. Especially interesting are the spectrograms made by treating uranous salts with nitric acid.

The spectrophotographs of chemical reactions show, invariably, that the changes produced in the spectra as one salt is transformed into another are gradual, whereas in changing the solvent this is not the case. *For instance, when uranyl nitrate is transformed into uranyl sulphate, the uranyl nitrate bands gradually shift into the sulphate position.* The same effect is produced when solutions are made containing different amounts of uranyl nitrate and uranyl sulphate. Further addition of sulphuric acid causes the bands to shift still more. An example is given where to a small amount of a solution of uranyl nitrate in nitric acid a large amount of sulphuric acid is added.

	Nitrate in nitric acid.	Same plus sulphuric acid.		Nitrate in nitric acid.	Same plus sulphuric acid.
a	4850	4930	*h*	3920	3980
b	4670	4750	*i*	3810	3870
c	[1]4520	[2]4560	*j*	3750	3770
d	4380	4380	*k*	3670	3660
e	4240	4240	*l*	3590	3560
f	4140	4100			
g	4050				

[1] Narrow. [2] Double.

It will be seen that the shifts in these cases are quite large, and the moving together of the *f* and *g* bands is especially remarkable. The chemical changes studied thus far spectroscopically have been in most cases confined to aqueous solutions. Changes effected in other solvents are usually smaller. For instance, the addition of sulphuric acid to a glycerol solution of uranous sulphate simply causes the g, h, and i bands to be shifted about 20 Ångström units to the violet. Similar changes are often produced by adding salts containing the cation of the acid. For instance, it has been found that the absorption spectra of uranyl chloride in a concentrated aqueous solution of aluminium chloride, or zinc chloride, or hydrochloric acid are very similar to that of uranyl and calcium chlorides in methyl alcohol, or of uranyl chloride in ethyl alcohol.

When nitric acid is added to an aqueous solution of uranous acetate, it is found that the oxidation of the uranous salt does not occur when small amounts of acid are added, but that in this case the uranous bands are shifted to the violet. The uranyl bands pass through several stages and change very greatly, indicating that the chemical reaction is quite complex.

The absorption spectra of uranous salts usually show the uranyl bands, and in some cases these are very strong. The question immediately arises as to whether the uranyl bands are common both to the uranyl and uranous salts. It seems probable that they are characteristic of only the uranyl salts, although this is not certain. Uranous salts have been obtained which show only a strong band appearing in about the same position as that of the blue-violet uranyl band, and this indicates that the presence of uranyl bands is due to the uranyl salt which has not been reduced. In most of the changes of solvent and salt it has been found possible to follow the individual uranyl bands throughout the reactions which took place, and this seems to indicate that the absorption is due to a system of some kind which preserves its entity throughout all these changes.

The gradual shift of the absorption bands as one salt of a metal is transformed into another salt by the addition of more and more free acid is very important.

The work already done in this laboratory on the absorption spectra of solutions, in which about five thousand solutions have now been studied, shows that any given series of absorption bands probably correspond to a definite chemical condition of the dissolved substance. When a salt is treated with a free acid the *absorption bands of some of the salts shift gradually over to the position occupied* by the bands corresponding to the new salt of the metal with the acid in question. *In an example of this kind the bands can be made to occupy any position between the initial and final positions, and it seems probable that when a salt of one acid is transformed in this way into a salt of another acid, there is a whole series of intermediate systems or compounds formed.* These are, for the most part, too unstable to be isolated by the methods at present at our disposal, but their action on light makes their existence in solution highly probable.

It is well known that our chemical equations represent, in general, only the beginning and end of chemical reactions, and tell us nothing about the intermediate stages of the reaction, which are, of course, the most interesting parts of the reaction. The results obtained in this work make it highly probable that *chemical reactions may sometimes be much more complex than would be indicated by the equations that we ordinarily use to express them.* When, for example, a nitrate is transformed into a sulphate, there seems to be a series of intermediate systems—nitrosulphates or sulphonitrates formed, about which we know nothing chemically, but whose existence is shown by a purely physical method—the action of these substances on light.

Whether we shall ever be able to deal with these substances chemically, it is impossible at present to predict on account of their comparative instability; the most hopeful methods of studying them being the physical chemical, which can investigate their properties while in solution in the different solvents.

Rise in temperature causes the general absorption of any salt in water to increase, and also causes the bands to broaden and become more intense.

The increase in the general absorption with rise in temperature is much greater for concentrated solutions. This also holds true for bands of the second type, and to a small extent for bands of the third type.

The presence of calcium and aluminium chlorides causes the chromium chloride bands to widen very unsymmetrically on the long wave-length edge with rise in temperature.

The uranyl chloride bands are shifted towards the red with rise in temperature. No shift for the uranyl nitrate could be detected. Uranyl nitrate, however, dissolved in strong nitric acid showed quite a large shift. The uranyl acetate and sulphate bands were slightly shifted.

No shift with rise in temperature was noticed for solutions of neodymium or erbium salts. When calcium chloride is present the neodymium chloride bands are, however, shifted, and the remarkable fact is observed that the bands then become fainter with rise in temperature. This latter phenomenon is considered to be very important, and it may be that the abnormal Zeeman effect observed by Becquerel is due to the presence of foreign compounds in the tysonite and xenotine crystals.

BEARING OF THE SOLVATE THEORY OF SOLUTION.

So much evidence has now been accumulated for the general correctness of the theory of solvation in solution, or combination of solvent and dissolved substance, that there can scarcely exist any reasonable doubt as to it representing a great truth of nature. Such being the case, the question arises whether it helps us in dealing with the phenomena presented by solutions?

When the study of the properties of solutions led to the discovery of the theory of electrolytic dissociation, it was soon recognized that this theory satisfied the conditions quantitatively only for *very dilute solutions.* The laws that hold for the properties of such solutions did not hold for solutions that were concentrated. Indeed, they did not apply to solutions of even moderate concentration; not to those solutions with which, for the most part, we actually have to deal in chemistry. If the solutions were fairly concentrated, the laws of osmotic pressure, of lowering of freezing-point, and lowering of vapor-tension did not hold at all.

Why this was true was not known. It was simply said that the laws of solutions do not hold for concentrated solutions, just as the laws of gases do not hold for concentrated gases, which, of course, was simply an analogy and explained nothing.

This failure of the gas laws to apply to even fairly concentrated solutions was held up by the early opponents of the theory of electrolytic dissociation as a weak point in this generalization as a general theory of solutions, and it must be confessed with some justice. We had here a theory of solutions which applied quantitatively only to *ideal solutions*, and did not accord with the facts for a single solution of even moderate concentration. Further, there was no reasonable explanation offered to account for this failure. In the case of gases, Van der Waal's equation adapted the simpler gas laws even to fairly concentrated gases, but in the case of solutions there was apparently no way to account for these discrepancies between the facts and theory; and thus the matter stood for quite a time.

The theory of electrolytic dissociation said simply this, that when molecules of acids, bases, and salts are brought into the presence of water, they are broken down into ions, to a greater or less extent depending upon the concentration of the solution. It did not recognize any combination of the solvent with the dissolved molecules or the ions.

The dilution of the solution was determined by the amount of dissolved substance in a given volume of the solution, *assuming that all of the liquid present was acting as solvent.*

We now know that this is not the case. A part of the solvent is, in most cases, combined with the dissolved substance and is not playing the rôle of solvent. There is, therefore, less solvent present than was supposed, and this is the same thing as to say that the *solution is more concentrated than it was thought to be from the way in which it was prepared.*

The amount of the combined solvent may be small, as in the cases where the dissolved substances do not crystallize with any of the solvent of crystallization. It may, however, be very large, as in the case of aluminium chloride in water at what is supposed to be twice normal concentration. Here about four-fifths of the water present is in combination with the dissolved substance, and the solution is really about *five times as concentrated as would be supposed from the amount of the salt present in a given volume.*

We thus see a reason for the failure of the gas laws to hold for concentrated solutions. In dilute solutions the amount of water combined with the dissolved substance, as compared with the total amount of water present, is practically negligible. In more concentrated solutions, however, the amount of the combined water may be a very appreciable part of the total water present, or in extreme cases, as that of aluminium chloride cited above, it may be several times the water that is present acting as solvent. *Concentrated solutions are thus more concentrated than we would suppose without the theory of solvation, and this accounts for the failure of the gas laws to apply to such solutions.*

A theory to be of greatest scientific value must, of course, be quantitative. While we have not been able, up to the present, to determine accurately the magnitude of the hydration in aqueous solutions, yet the approximate composition of the hydrates formed by a large number of substances at various concentrations has been worked out; so that the theory of solvation, as far as aqueous solutions are concerned, is now on approximately a quantitative basis.

The question arises, in this connection, why is a true and adequate theory of solutions of such importance not only for physical or general chemistry, but for so many branches of science? The answer is to be found in the importance of solutions, in the broad sense of that term, for the natural sciences. The one reason above all others why physical chemistry has reached out into so many branches of science, is that it deals scientifically with solutions. Into what branch of science do solutions not enter? Chemistry is essentially a science of solutions. Physics depends upon solutions for many of its more important developments. Geology deals with the results of solution not only in the sedimentary rocks, but in the fused magmas. We might almost say without solution no geology.

When we turn to the biological sciences we find many of them fundamentally connected with the science of solutions. This is especially true of physiology, as Loeb has shown. It is almost equally true of pharmacology; and solutions are of fundamental importance for physiological chemistry, physiological botany, and pathology. Indeed, about the only branch of natural science that seems to be independent of solutions is astronomy.

We can see from the above why a theory that accounts for the properties of solutions in general is of fundamental importance for the development of the natural sciences.

A word as to the relation between the *solvate theory* and the *theory of electrolytic dissociation*, lest some one should suppose that they are antagonistic. The theory of electrolytic dissociation, as has been pointed out, simply says that molecules of electrolytes in the presence of a dissociating solvent are broken down more or less into ions. It does not raise any question as to whether the ions are or are not combined with any of the solvent. It has been shown that while this theory is necessary to account for the properties of solutions, and is accepted without question by practically all chemists of reputation, it is not sufficient to account for the properties especially of concentrated solutions.

We must go farther than recognize dissociation and determine its magnitude. We must find out the condition of the ions in solution after they are formed, and of the undissociated molecules. This the theory of solvation aims to do. It attempts to answer the question whether the molecules or ions are combined with any part of the solvent, and, if so, with how much. The theory of solvation thus supplements the theory of ionization, and when the former is upon as good a quantitative basis as the latter, we shall have a satisfactory theory of solution.

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Conductivity and Viscosity in Mixed Solvents. A Study of the Conductivity and Viscosity of Solutions of Certain Electrolytes in Water, Methyl Alcohol, Ethyl Alcohol, and Acetone; and in Binary Mixtures of These Solvents. By Harry C. Jones and C. F. Lindsay, C. G. Carroll, H. P. Bassett, E. C. Bingham, C. A. Rouiller, L. McMaster, W. R. Veazey. Carnegie Institution of Washington Publication No. **80** (1907).

The Absorption Spectra of Solutions of Certain Salts of Cobalt, Nickel, Copper, Iron, Chromium, Neodymium, Praseodymium, and Erbium in Water, Methyl Alcohol, Ethyl Alcohol, and Acetone, and in Mixtures of Water with the Other Solvents. By Harry C. Jones and John A. Anderson. Carnegie Institution of Washington Publication No. **110** (1909).

A Study of the Absorption Spectra of Solutions of Certain Salts of Potassium, Cobalt, Nickel, Copper, Chromium, Erbium, Praseodymium, Neodymium, and Uranium, as affected by Chemical Agents and by Temperature. By Harry C. Jones and W. W. Strong. Carnegie Institution of Washington Publication No. **130.**

DESCRIPTION OF THE PLATES.

In the description of the plates there is usually given the time of exposure and the quantity of current flowing through the Nernst glower. Almost invariably the amount of light entering any solution is the same for every strip on any spectrogram. For different spectrograms the amount of light varies according to the opacity of the solution. In many cases where the solutions absorbed completely in the ultra-violet, an exposure was made in the extreme ultra-violet only to the spark; the solution not being in the path of the beam of light. These spark lines were used as wave-length references. In making an exposure to a reference line the film holder was never moved, so that there was no possibility of shifts. In a few cases there are streaks running parallel to the strips. This is due to bubbles or some other obstacles in the solution opaque to the light. Glycerol solutions present many difficulties of this kind. One of these is the inequalities in a glycerol solution produced by heating. One way of making the light illumination across any strip more uniform, is by moving the solution back and forth in the path of the beam of light.

PLATE 1. *A*. Potassium Chromate. Depth of cell constant, 3 mm. Concentrations, 2, 1.5, 1, 0.66, 0.46, 0.33 and 0.25 normal.

B. Potassium Chromate. Depth of cell constant, 3 mm. Concentrations, 0.25, 0.19, 0.12, 0.08, 0.06, 0.04, and 0.031 normal.

PLATE 2. *A*. Potassium Chromate. Depth of cell constant, 3 mm. Concentrations, 0.031, 0.023, 0.0156, 0.0103, 0.0072, 0.0052, and 0.004 normal.

B. Potassium Chromate. Depth of cell constant, 3 mm. Concentrations, 0.004, 0.003, 0.002, 0.0013, 0.0009, 0.00065, and 0.0005 normal.

PLATE 3. *A*. Potassium Chromate, Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm. Concentrations, 2. 1.5, 1, 0.66, 0.46, 0.33, and 0.25 normal.

B. Potassium Chromate, Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm. Concentrations, 0.25, 0.19, 0.12, 0.08, 0.06, 0.04, and 0.031 normal.

PLATE 4. *A*. Potassium Chromate, Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm. Concentrations, 0.031, 0.023, 0.0156, 0.0103, 0.0072, 0.0052, and 0.004 normal.

B. Potassium Chromate, Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm. Concentrations, 0.004, 0.003, 0.002, 0.0013, 0.0009, 0.00065, and 0.0005 normal.

PLATE 5. *A*. Potassium Dichromate, Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm. Concentrations, 0.33, 0.25, 0.16, 0.11, 0.077, 0.055, and 0.042 normal.

B. Potassium Dichromate. Depth of cell constant, 3 mm. Concentrations, 0.33, 0.25, 0.16, 0.11, 0.077, 0.055, and 0.042 normal.

PLATE 6. *A*. Potassium Dichromate. Depth of cell constant, 3 mm. Concentrations, 0.042, 0.031, 0.02, 0.014, 0.0096, 0.007, and 0.0052 normal.

B. Potassium Dichromate. Depth of cell constant, 3 mm. Concentrations, 0.005, 0.004, 0.0025, 0.0017, 0.0012, 0.009, and 0.0006 normal.

PLATE 7. *A*. Potassium Dichromate, Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm. Concentrations, 0.041, 0.031, 0.02, 0.014, 0.0096, 0.007, and 0.0052 normal.

B. Potassium Dichromate, Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm. Concentrations, 0.005, 0.004, 0.0025, 0.0017, 0.0012, 0.009, and 0.0006 normal.

PLATE 8. *A*. Potassium Ferrocyanide. Depth of cell constant, 3 mm. Concentrations, 0.5, 0.37, 0.25, 0.17, 0.12, 0.09, and 0.063 normal.

B. Potassium Ferrocyanide. Depth of cell constant, 3 mm. Concentrations, 0.06, 0.046, 0.032, 0.021, 0.015, 0.011, and 0.008 normal.

PLATE 9. *A*. Potassium Ferrocyanide, Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm. Concentrations, 0.5, 0.37, 0.25, 0.17, 0.12, 0.09, and 0.063 normal.

B. Potassium Ferrocyanide, Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm. Concentrations, 0.06, 0.046, 0.032, 0.021, 0.015, 0.011, and 0.008 normal.

PLATE 10. *A*. Potassium Ferricyanide. Depth of cell constant, 3 mm. Concentrations, 1, 0.75, 0.5, 0.33, 0.23, 0.166, and 0.125 normal.

B. Potassium Ferricyanide. Depth of cell constant, 3 mm. Concentrations, 0.125, 0.094, 0.0625, 0.0425, 0.029, 0.0208, and 0.0156 normal.

PLATE 11. *A*. Potassium Ferricyanide. Depth of cell constant, 3 mm. Concentrations, 0.0156, 0.0118, 0.0078, 0.0053, 0.0036, 0.0026, and 0.0019 normal.

B. Potassium Ferricyanide. Depth of cell constant, 3 mm. Concentrations, 0.0019, 0.0013, 0.001, 0.0066, 0.00045, 0.00032, and 0.00024 normal.

PLATE 12. *A*. Potassium Ferricyanide, Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm. Concentrations, 1, 0.75, 0.5, 0.33, 0.23, 0.166, and 0.125 normal.

B. Potassium Ferricyanide, Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm. Concentrations, 0.125, 0.094, 0.062, 0.042, 0.029, 0.021, and 0.0156 normal.

PLATE 13. *A*. Cobalt Chloride in Water. 2.37 normal concentration. 1.3 mm. depth of cell. Temperatures, 2°, 14°, 30°, 45°, 60°, 70°, 81° C. Length of exposure, 3 minutes.

B. Cobalt Chloride. 0.315 normal concentration. 10.4 mm. depth of cell. Temperatures, 2°, 14°, 30°, 44°, 60°, 75°, 81° C. Length of exposure, 3 minutes.

PLATE 14. *A*. Cobalt Chloride. 0.04 normal concentration. 83 mm. depth of cell. Temperatures, 14°, 30°, 44°, 58°, 72°, 80° C. Length of exposure, 4 minutes.

B. Cobalt Nitrate. 2.3 normal concentration, 2 mm. depth of cell. Temperatures, 2°, 14°, 28°, 45°, 60°, 75°, 85° C. Length of exposure, 3 minutes.

PLATE 15. *A*. Cobalt Chloride. 0.125 normal. 12 mm. depth of cell. Temperatures, 5°, 20°, 38°, 52°, 64°, and 83° C. Length of exposure, 4 minutes.

B. Cobalt Nitrate. 0.29 normal. 3 mm. depth of cell. Temperatures, 13°, 27°, 42°, 61°, 73°, and 85° C. Length of exposure, 2 minutes.

PLATE 16. *A*. Cobalt Sulphate. 1.0 normal. 3 mm. depth of cell. Temperatures, 6°, 19°, 36°, 49°, 64°, and 80° C. Length of exposure, 2 minutes.

B. Nickel Sulphate. 2.0 normal. 3 mm. depth of cell. Temperatures, 5°, 19°, 32°, 47°, 61°, 72°, and 81° C. Length of exposure, 2 minutes.

PLATE 17. *A*. Cobalt Acetate. 1.0 normal. 3 mm. depth of cell. Temperatures, 4°, 18°, 32°, 50°, 64°, 80° C. Length of exposure, 2 minutes.

B. Cobalt Acetate. 0.125 normal. 24 mm. depth of cell. Temperatures, 7°, 27°, 47°, 61°, 73°, and 81° C. Length of exposure, 2 minutes.

PLATE 18. *A*. Cobalt and Calcium Chlorides. Cobalt Chloride, 0.237 normal; Calcium Chloride, 4.14 normal. Temperatures, 2°, 15°, 30°, 42°, 58°, 75°, 86° C. Length of exposure, 3 minutes. 3 mm. depth of cell.

B. Cobalt and Aluminium Chlorides. Cobalt Chloride, 0.221 normal; Aluminium Chloride, 2.75 normal. Temperatures, – 1.0°, 12°, 32°, 45°, 60°, 72°, and 87° C. Length of exposure, 3 minutes.

Plate 19. *A*. Cobalt and Aluminium Chlorides. Cobalt Chloride, 0.00316 normal; Aluminium Chloride, 3.06 normal. Depth of cell, 150 mm. Temperatures, 3°, 18°, 41°, 55°, 68°, and 85° C. Length of exposure, 2 minutes.

B. Cobalt and Calcium Chlorides. Cobalt Chloride, 0.00948 normal; Calcium Chloride, 4.6 normal. Depth of cell, 50 mm. Temperatures, 1°, 20°, 32°, 45°, 58°, 75°, 88° C. Length of exposure, 3 minutes.

Plate 20. *A*. Cobalt Sulphocyanate. 2 normal. 1 mm. depth of cell. Temperatures, 3°, 18°, 31°, 45°, 60°, and 80° C. Length of exposure, 3 minutes.

B. Cobalt Sulphocyanate. 0.25 normal. 8 mm. depth of cell. Temperatures, 6°, 20°, 33°, 47°, 59°, 73°, and 80° C. Length of exposure, 2 minutes.

Plate 21. *A*. Nickel Chloride. 0.332 normal. 16 mm. depth of cell. 2 minutes exposure. Temperatures, 5°, 19°, 33°, 45°, 60°, 71°, 82° C.

B. Nickel Chloride. 2.66 normal. 2 mm. depth of cell. 2 minutes exposure. Temperatures, 5°, 18°, 30°, 44°, 57°, 75°, 85° C.

Plate 22. *A*. Nickel Acetate. 0.5 normal. 9 mm. depth of cell. 2 minutes exposure. Temperatures, 6°, 23°, 38°, 52°, 64°, 74°, 84° C.

B. Nickel Acetate. 0.5 normal. 3 mm. depth of cell. 2 minutes exposure. Temperatures, 5°, 20°, 33°, 46°, 60°, 71°, 81° C.

Plate 23. *A*. Copper Bromide. 2.06 normal. 1 mm. depth of cell. Length of exposure, 2 minutes. Temperatures, 6°, 17°, 30°, 45°, 71° C.

B. Copper Bromide. 0.25 normal. 8 mm. depth of cell. Length of exposure, 2 minutes. Temperatures, 6°, 17°, 31°, 46°, 59°, 71°, 85° C.

Plate 24. *A*. Copper Nitrate. 4.04 normal. 2 mm. depth of cell. Length of exposure, 2 minutes. Temperatures, 5°, 15°, 30°, 45°, 60°, 76°, 87° C.

B. Copper Nitrate. 0.505 normal. 16 mm. depth of cell. Length of exposure, 3 minutes. Temperatures, 1°, 15°, 30°, 45°, 60°, 75°, 82° C.

Plate 25. *A*. Chromium Nitrate. 0.754 normal. 3 mm. depth of cell. Length of exposure, 2 minutes. Temperatures, 7°, 18°, 32°, 46°, 59°, 73°, and 84° C.

B. Copper Nitrate. 4.04 normal. 3 mm. depth of cell. Length of exposure, 3 minutes. Temperatures, 4°, 16°, 33°, 46°, 59°, 71°, 82° C.

Plate 26. *A*. Chromium Nitrate. 0.754 normal. 3 mm. depth of cell. 3 minutes exposure. Temperatures, 5°, 17°, 32°, 45°, 60°, 71°, 81° C.

B. Chromium Nitrate. 0.094 normal. 24 mm. depth of cell. 3 minutes exposure. Temperatures, 7°, 17°, 33°, 44°, 59°, 69° C.

Plate 27. *A*. Chromium Chloride. 0.125 normal Chromium Chloride. 2.28 normal Aluminium Chloride. 9 mm. depth of cell. Length of exposure, 4 minutes. Temperatures, 6°, 19°, 36°, 51°, 66°, 81° C.

B. Chromium Chloride. 0.125 normal Chromium Chloride. 3.45 normal Calcium Chloride. 9 mm. depth layer. 5 minutes exposure. Temperatures, 6°, 19°, 31°, 45°, 64° C.

Plate 28. *A*. Chrome Alum $KCr(SO_4)_2$. 0.0083 normal. 9 mm. depth of cell. 3 minutes exposure. Temperatures, 5°, 18°, 33°, 46°, 61°, 71°, 83° C.

B. Chromium Sulphate. 0.125 normal. 3 mm. depth of cell. 4 minutes exposure. Temperatures, 5°, 20°, 37°, 51°, 66°, 82° C.

Plate 29. *A*. Strip 1. $ErCl_3$ in Glycerol. Temperature 15° C.
Strip 2. $ErCl_3$ in Glycerol. Temperature 200° C.
Strip 3. $U(SO_4)_2$ in Glycerol. Temperature 15° C.
Strip 4. $U(SO_4)_2$ in Glycerol. Temperature 200° C.

B. Strip 1. $NdCl_3$ in Glycerol. Temperature 15° C. Concentration 0.02 normal.
Strip 2. $NdCl_3$ in Glycerol. Temperature 200° C. Concentration 0.02 normal.
Strip 3. $NdCl_3$ in Glycerol. Temperature 15° C. Concentration 0.15 normal.
Strip 4. $NdCl_3$ in Glycerol. Temperature 200° C. Concentration 0.15 normal.
Strip 5. $ErCl_3$ in Glycerol. Temperature 15° C.
Strip 6. $ErCl_3$ in Glycerol. Temperature 200° C.

PLATE 30. *A.* Neodymium Bromide in Water. 1.66 normal. 45.6 mm. depth of cell. Temperatures, 6°, 20°, 33°, 47°, 62°, 73°, and 82° C.

B. Erbium Chloride in Water. 0.94 normal. 48 mm. depth of cell. Temperatures, 7°, 17°, 29°, 46°, 60°, 70°, 80° C.

PLATE 31. *A.* Praseodymium Chloride. 2.56 normal. 3 mm. depth of cell. Temperatures, 7°, 23°, 40°, 52°, 68°, 83° C.

B. Praseodymium Chloride. 0.043 normal. 196 mm. depth of cell. Temperatures, 7°, 20°, 36°, 51°, 66°, 81° C.

PLATE 32. *A.* Praseodymium Nitrate. 2.6 normal. 46.5 mm. depth of cell. Temperatures, 6°, 19°, 47°, 70°, 90° C.

B. Praseodymium Chloride. 2.56 normal. 48 mm. depth of cell. Temperatures, 7°, 20°, 35°, 51°, 66°, 84° C.

PLATE 33. *A.* Praseodymium Nitrate. 2.6 normal. 3 mm. depth of cell. Temperatures, 6°, 16°, 34°, 46°, 58°, 70°, 82° C.

B. Neodymium Nitrate. 2.15 normal. 3 mm. depth of cell. Temperatures, 4°, 17°, 29°, 43°, 58°, 71°, 84° C.

PLATE 34. *A.* Neodymium Chloride in Glycerol. Depth of cell constant, 9 mm. Concentrations, 0.84, 0.63, 0.42, 0.28, 0.196, and 0.105 normal.

B. Neodymium Chloride in Glycerol. Depth of cell constant, 3 mm. Concentrations, 0.105, 0.143, 0.196, 0.28, 0.42, 0.63, and 0.84 normal.

PLATE 35. *A.* Neodymium Chloride in Glycerol. Test for Beer's Law. Depth of cell, 3, 4, 6, 9, 13, 18, 24 mm. Concentrations, 0.84, 0.63, 0.42, 0.28, 0.196, 0.143, and 0.105 normal.

B. Neodymium Chloride in Glycerol. Constant depth of cell, 24 mm. Concentrations, 0.105, 0.143, 0.196, 0.28, 0.42, 0.63, and 0.84 normal.

PLATE 36. *A.* Neodymium Chloride in Glycerol and Water. Depth of cell, 2.2 mm. Concentrations of Neodymium Chloride, 0.84, 0.80, 0.76, 0.67, and 0.59 normal. Percentages of Water, 0, 5, 10, 20, 30, 60, and 90.

B. Neodymium Chloride in Glycerol and Water. Depth of cell, 32.5 mm. Concentrations, 0.59, 0.67, 0.76, 0.80, and 0.84 normal. Percentages of Water, 90, 60, 30, 20, 10, 5, and 0.

PLATE 37. *A.* Neodymium Chloride in Water. 3.4 normal. 12 mm. depth of cell. Temperatures, 11°, 22°, 33°, 45°, 59°, 73°, and 85° C.

B. Neodymium Chloride in Water. 0.17 normal. 196 mm. depth of cell. Temperatures, 5°, 16°, 28°, 42°, 59°, 72°, and 82° C.

PLATE 38. *A.* Neodymium Chloride in Water. 3.4 normal. 43 mm. depth of cell. Temperatures, 6°, 21°, 36°, 47°, 60°, 77°, and 83° C.

B. Neodymium Nitrate in Water. 2.96 normal. 38.5 mm. depth of cell. Temperatures, 7°, 17.5°, 30°, 44.5°, 59°, 70°, and 82° C.

PLATE 39. *A.* Neodymium Bromide. 1.66 normal. 6 mm. depth of cell. Temperatures, 4.5°, 20°, 36°, 50°, 68°, and 83° C.

B. Neodymium Bromide. 0.055 normal. 197.4 mm. depth of cell. Temperatures, 5.5°, 16.5°, 29°, 42.5°, 55°, 68°, and 84° C.

PLATE 40. *A.* Neodymium and Calcium Chlorides in Water. 2.05 normal Neodymium Chloride added to 4.6 normal Calcium Chloride. Temperatures, 6°, 17°, 31°, 49°, 63°, 74°, and 82° C.

B. Neodymium Nitrate in Water. 0.036 normal. 197 mm. depth of cell. Temperatures, 9°, 22°, 42°, 56°, 69°, 78° C.

PLATE 41. *A.* Neodymium Acetate to which HNO_3 is added. Depth of cell, 30 mm. Concentration of Neodymium Acetate, 0.041 normal. Concentrations of HNO_3, 0.117, 0.234, 0.585, 1.17, 4.09, 8.18, and 16.36.

B. Neodymium Acetate in Water. Concentration constant, 0.041 normal. Depth of cell, 1, 2, 3, 6, 14, and 34 mm.

PLATE 42. *A.* Neodymium Chloride in Glycerol. 0.15 normal. Temperatures, 20°, 60°, 110°, 150°, 180° C.

B. Neodymium Nitrate in Concentrated Nitric Acid. Concentration, 0.4 normal. Depth of cell, 0.2, 0.8, 2, 6, 16, and 32 mm.

PLATE 43. *A*. Neodymium Chloride in Water and Ethyl Alcohol. Solution contained 8 per cent water.

Strips 1, 2, 3, 4, Beer's Law. Concentrations of $NdCl_3$, 0.5, 0.3, 0.1, and 0.05 normal.

Strips 5, 6, 7. Concentration, 0.5 normal. Depth of cell changed.

B. Neodymium Acetate in Water. Strip 1 represents the Neodymium Acetate solution in Water. Succeeding strips show the effect of adding more and more Hydrobromic Acid.

PLATE 44. *A*. Neodymium Acetate in Water. 0.041 normal. Strip 1, pure aqueous solution. Strip 2, the same to which one drop of HCl has been added. Succeeding strips represent the addition of more and more HCl.

B. Mixtures of Neodymium Acetate and Neodymium Chloride in Water. Strip 1, all Neodymium Acetate. Strip 7, all Neodymium Chloride.

PLATE 45. *A*. Neodymium Acetate in Water. Depth of cell, 30 mm. Concentration of Acetate, 0.041 normal. Concentration of Hydrochloric Acid, 0.113, 0.226, 0.566, 1.13, 3.95, 7.91, and 15.82.

B. Neodymium Citrate in Water. Depth of cell, 30 mm. Strip 2 and succeeding strips show the effect of the addition of HCl.

PLATE 46. *A*. Strip 1. 0.15 normal $NdCl_3$ and $AlCl_3$ in Glycerol at 10° C.

Strip 2. Same at 200° C.

Strip 3. 0.15 normal $NdCl_3$ and $CaCl_2$ in Glycerol at 10° C.

Strip 4. Same at 200° C.

Strip 5. Uranous and Aluminium Chlorides in Water at 10° C.

Strip 6. Same at 100° C.

B. Neodymium Acetate in Water. 0.041 normal. 9 mm. depth of cell. Concentrations of HNO_3, 0.117, 0.234, 0.585, 1.17, 4.09, 8.18, and 16.36 normal. The reaction took place between the second and third strips in this case.

PLATE 47. *A*. Strip 1. Neodymium Chloride in Water.

Strip 2. Same solution to which about ten times its volume of strong HCl has been added.

Strip 3. Neodymium Chloride in HCl at 10° C.

Strip 4. The same at 100° C.

Strip 5. Uranous Acetate at 10° C.

Strip 6. The same at 100° C.

B. Strip 1. Uranyl Nitrate in Strong Nitric Acid at 10° C.

Strip 2. The same at 100° C.

Strip 3. The same at 10° C.

Strip 4. Neodymium Nitrate in Nitric Acid at 10° C.

Strip 5. The same at about 90° C.

Strip 6. Neodymium Chloride in Water.

PLATE 48. *A*. Uranyl Chloride in Water. Beer's Law. Concentrations, 0.12, 0.16, 0.2, 0.33, 0.5, 0.75, and 1.0 normal. Depths of cell, 24, 18, 13, 9, 6, 4, and 3 mm.

B. Uranyl Chloride in Water. Depth of cell constant, 3 mm. Concentrations, 0.12, 0.16, 0.2, 0.33, 0.5, 0.75, and 1.0 normal.

PLATE 49. *A*. Uranyl Chloride in Water. Concentration constant, 0.2 normal. Depth of cell, 3, 6, 12, 24, and 35 mm. This plate is to show how much weaker the uranyl bands are in a pure aqueous solution, compared with a solution containing some other salt or hydrochloric acid.

B. Uranyl and Aluminium Chlorides in Water. Concentration Uranyl Chloride, 0.2 normal, Aluminium Chloride, 2.43 normal. Depths of cell, 3, 6, 12, 24, and 35 mm.

PLATE 50. *A*. Uranyl and Zinc Chlorides in Water. Concentration Uranyl Chloride, 0.2 normal. Zinc Chloride almost saturated. Depths of cell, 3, 6, 12, 24, and 35 mm.

B. Uranyl Chloride and Hydrochloric Acid. Concentration Uranyl Chloride, 0.2 normal; Hydrochloric Acid very strong. Depth of cell, 3, 6, 12, 24, and 35 mm.

PLATE 51. *A*. Uranyl and Aluminium Chlorides in Water. Depth of cell constant, 6 mm. Concentration of Uranyl Chloride constant at 0.25 normal. Concentrations of Aluminium Chloride, 2.02, 1.61, 1.21, 0.81, 0.4, and 0.

B. Uranyl and Aluminium Chlorides in Water. Depth of cell constant, 3 mm. Concentration of Uranyl Chloride constant at 0.25 normal. Concentrations of Aluminium Chloride, 2.02, 1.61, 1.21, 0.81, 0.4, and 0.

PLATE 52. *A*. Uranyl and Calcium Chlorides in Water. Depth of cell constant, 13 mm. Concentration of Uranyl Chloride constant at 0.25 normal. Concentrations of Calcium Chloride.

B. Uranyl and Calcium Chlorides in Water. Depth of cell constant, 3 mm. Concentration of Uranyl Chloride constant at 0.25 normal. Concentrations of Calcium Chloride.

PLATE 53. *A*. Uranyl Chloride in Methyl Alcohol. Beer's Law. Depths of cell, 24, 19, 15, 12, 9.5, 7.5, and 6 mm. Concentrations, 0.0625, 0.079, 0.10, 0.125, 0.158, 0.20, and 0.25 normal.

B. Uranyl Chloride in Methyl Alcohol. Depth of cell constant, 6 mm. Concentrations 0.0625, 0.079, 0.10, 0.125, 0.158, 0.20, and 0.25 normal.

PLATE 54. *A*. Uranyl and Calcium Chlorides in Methyl Alcohol. Concentration Uranyl Chloride, 0.125 normal. Depth of cell, 6 mm. Concentrations of Calcium Chloride, 0.0, 0.144, 0.29, 0.43, 0.57, 0.72, and 0.9 normal.

B. Uranyl and Calcium Chlorides in Methyl Alcohol. Concentration of Uranyl Chloride, 0.125 normal. Depth of cell, 3 mm. Concentrations of Calcium Chloride, 0.0, 0.144, 0.29, 0.43, 0.57, 0.72, and 0.9 normal.

PLATE 55. *A*. Uranyl Chloride in Methyl Alcohol. Depth of cell, 15 mm. Concentrations, 0.0625, 0.079, 0.10, 0.125, 0.158, 0.20, and 0.25 normal.

B. Uranyl Nitrate in Methyl Alcohol. Depth of cell constant, 15 mm. Concentrations, 0.05, 0.063, 0.079, 1.0, 1.24, 1.58, 0.2 normal.

PLATE 56. Uranyl Chloride in Methyl Alcohol and Water. Concentration of Uranyl Chloride, 0.1 normal. Percentages of Water, 100, 50, 40, 32, 24, 16, and 8.

A. Depth of cell, 16.7 mm.

B. Depth of cell, 6 mm.

PLATE 57. *A*. Uranyl Chloride in Ethyl Alcohol. Depth of cell constant, 15 mm. Concentrations of Uranyl Chloride, 0.0625, 0.079, 0.1, 0.125, 0.158, 0.2, and 0.25 normal.

B. Uranyl Chloride in Methyl Alcohol and Water. Depth of cell constant, 6 mm. Concentration of Uranyl Chloride constant. Percentages of Water, 100, 50, 40, 32, 24, 16, and 8.

PLATE 58. *A*. Uranyl Chloride in Ethyl Alcohol. Concentrations, 0.0625, 0.079, 0.1, 0.125, 0.158, 0.2, and 0.25 normal. Depths of cell, 24, 19, 15, 12, 9.5, 7.5, and 6 mm.

B. Uranyl Chloride in Ethyl Alcohol. Depth of cell constant, 6 mm. Concentrations, 0.0625, 0.079, 0.1, 0.125, 0.158, 0.2, and 0.25 normal.

PLATE 59. *A*. Uranyl Chloride in Glycerol. Depth of cell constant, 10 mm. Concentrations, 0.176, 0.132, 0.088, 0.059, 0.041, 0.030, and 0.022 normal.

B. Uranyl Chloride in Glycerol. Depth of cell constant, 5 mm. Concentrations, 0.176, 0.132, 0.088, 0.059, 0.041, 0.030, and 0.022 normal.

PLATE 60. Uranyl Chloride in Mixtures of Glycerol and Methyl Alcohol. Concentration of Uranyl Chloride constant, 0.176 normal. Percentages of Methyl Alcohol, 0, 15, 30, 45, 60, 75, and 90.

A. Depth of cell, 25 mm.

B. Depth of cell, 3 mm.

PLATE 61. *A*. Uranyl Chloride in Water. Concentration 1.0 normal. Depth of cell, 3 mm. Temperatures, 6°, 18°, 34°, 52°, 68°, and 82° C.

B. Uranyl Chloride in Water. Concentration, $\frac{1}{64}$ normal. Depth of cell, 196 mm. Temperatures, 6°, 18°, 29°, 44°, 59°, 71°, and 81° C.

PLATE 62. *A.* Uranyl Nitrate in Water. Depth of cell constant, 3 mm. Concentrations, 0.19, 0.25, 0.37, 0.5, 0.75, 1.12, and 1.5 normal.

B. Uranyl Nitrate in Water. Concentration constant, 0.022 normal. Depth of cell, 3, 4, 6, 9, 12, 18, and 24 mm. Since Beer's law holds this is equivalent to keeping the depth of cell constant and changing the concentration.

PLATE 63. *A.* Uranyl Nitrate in Water. Concentrations, 0.187, 0.25, 0.375, 0.5, 0.75, 1.125, and 1.5 normal. Depth of cell for red, 15 mm.; for the ultra-violet, 3 mm.

B. Uranous Chloride in Water. Depth of cell, 2 mm. Temperatures, 8°, 17°, 33°, 48°, 62°, 73°, and 80° C.

PLATE 64. *A.* Uranyl Nitrate in Water. Beer's Law. Depth of cell, 24, 18, 13, 9, 6, 4, 3 mm. Concentrations, 0.187, 0.25, 0.375, 0.5, 0.75, 1.125, and 1.5 normal.

B. Uranyl Nitrate in Water. Depth of cell, 24, 18, 13, 9, 6, 4, and 3 mm. Concentrations, 0.0234, 0.0312, 0.047, 0.0625, 0.094, 0.14, and 0.1875 normal.

PLATE 65. *A.* Strip 1. Uranyl Nitrate in Water. 1.1 normal. Depth of layer, 3 mm.
Strip 2. Is identical with strip 1.
Strip 3. Water is added so as to make the depth of cell 380 mm.
Strip 4. Uranyl Sulphate. 0.75 normal. Depth of layer, 4 mm.
Strip 5. Water is added so as to make the depth of cell 380 mm.
Strip 6. Uranyl Acetate. 0.188 normal solution.
Strip 7. Water is added so as to make the depth of cell 380 mm.

B. Strip 1. Uranyl Sulphate in Water. 1.0 normal. Depth of layer, 3 mm.
Strip 2. Uranyl Acetate in Water. 0.25 normal. Depth of layer, 12 mm.
Strip 3. Uranyl Nitrate in Water. 0.75 normal. Depth of layer, 4 mm.
Strip 4. Uranyl Sulphate in Water. 0.75 normal. Depth of layer, 4 mm.

PLATE 66. Uranyl Nitrate in Methyl Alcohol and Water. Concentration of Uranyl Nitrate constant at 0.1 normal. Percentages of Water, 50, 40, 32, 24, 16, 8, and 0.

A. Depth of cell, 15 mm.
B. Depth of cell, 6 mm.

PLATE 67. *A.* Uranyl Nitrate in Methyl Alcohol, Beer's Law. Depth of cell, 6, 7.5, 9.5, 12, 15, 19, and 24 mm. Concentrations, 0.2, 0.16, 0.127, 0.10, 0.08, 0.063, and 0.033 normal.

B. Uranyl Nitrate in Methyl Alcohol. Depth of cell constant, 3 mm. Concentrations, 0.05, 0.063, 0.079, 0.10, 0.124, 0.158, and 0.2 normal.

PLATE 68. *A.* Uranyl Nitrate in Ethyl Alcohol. Beer's Law. Depth of cell, 6, 7.5, 9.5, 12, 15, 19, and 24 mm. Concentrations, 0.2, 0.16, 0.127, 0.10, 0.08, 0.063, and 0.033 normal.

B. Depth of cell constant, 15 mm. Concentrations, 0.033, 0.063, 0.08, 0.10, 0.127, 0.16, and 0.2 normal.

PLATE 69. Strip 1. Uranyl Nitrate in Glycerol.
Strip 2. Uranyl Nitrate in three parts of Glycerol to one of Water.
Strip 3. Uranyl Nitrate in two parts of Glycerol to two of Water.
Strip 4. Uranyl Nitrate in one part of Glycerol to three of Water.
Strip 5. Uranyl Nitrate in one part of Glycerol to three of Acetone.
Strip 6. Uranyl Nitrate in one part of Glycerol to three of Alcohol.
A. Depth of cell, 25 mm.
B. Depth of cell, 6 mm.

PLATE 70. *A.* This Spectrogram gives the Absorption Spectra of a solution of Uranous Chloride in Hydrochloric Acid to which Acetone was added to increase the cell depth. Depth of cell, 5, 6, 8, 10, 15, and 30 mm.

B. Uranyl Nitrate in Nitric Acid. 0.12 normal. Depth of cell, 1.2, 2, 3, 4, 6, 11, and 24 mm.

PLATE 71. *A*. Uranyl Nitrate in Water. $\frac{1}{64}$ normal. Depth of cell, 196 mm. Temperatures, 9.5°, 23°, 46°, 59°, 70°, and 79° C.

B. Uranyl Nitrate in Water. 1.0 normal. Depth of cell, 3 mm. Temperatures, 11°, 24.5°, 40°, 53.5°, 67.5°, and 82° C.

PLATE 72. *A*. Uranyl Bromide in Water, Beer's Law. Depth of cell, 24, 18, 12, 9, 6, 4, and 3 mm. Concentrations, 0.16, 0.2, 0.25, 0.33, 0.5, 0.75, and 1.0 normal.

B. Uranyl Bromide in Water. Depth of cell constant, 3 mm. Concentrations, 0.16, 0.2, 0.25, 0.33, 0.5, 0.75, and 1.0 normal.

PLATE 73. *A*. Uranyl Sulphate in Water. 1.0 normal. Depth of cell, 3 mm. Temperatures, 5°, 19°, 32°, 54°, 67°, and 84° C.

B. Uranyl Sulphate in Water. 0.0156 normal. Depth of cell, 196 mm. Temperatures, 6°, 19°, 36°, 51°, 67°, and 81° C.

PLATE 74. *A*. Uranyl Acetate in Water, Beer's Law. Depth of cell, 24, 18, 12, 9, 6, 4 and 3 mm. Concentrations, 0.031, 0.042, 0.062, 0.083, 0.125, 0.18, and 0.25 normal.

B. Uranyl Acetate in Water. Concentration constant, 0.031 normal. Depth of cell, 3, 4, 6, 9, 12, 18, and 24 mm.

PLATE 75. *A*. Uranyl Acetate in Methyl Alcohol, Beer's Law. Concentrations, 0.06, 0.07, 0.10, 0.12, 0.16, 0.20, and 0.25 normal. Depth of cell, 24, 19, 15, 12, 9.5, 7.5, and 6 mm.

B. Depth of cell constant, 6 mm. Concentrations, 0.06, 0.07, 0.10, 0.12, 0.16, 0.20, and 0.25 normal.

PLATE 76. *A*. Uranyl Chloride in Water. Concentration, 1.0 normal. Depth of cell, 1, 2, 4, 18, 16, 32, and 45 mm.

B. Uranyl Acetate in Water. 0.25 normal. Depth of cell, 3 mm. Temperatures, 5°, 19°, 32.5°, 47.5°, 61°, 70.5°, and 84° C.

PLATE 77. Uranyl Nitrate in Water.

A. Effect of adding Acetic Acid on the Uranyl Nitrate bands.

B. Effect of adding Hydrochloric Acid on the Uranyl Nitrate bands.

PLATE 78. *A*. Uranous Bromide in Methyl Alcohol. Depth of cell, 3, 6, 11, and 16 mm.

B. Uranyl Nitrate in Water to which Hydrobromic Acid is added.

C. Mixtures of Uranyl Nitrate and Uranyl Sulphate in Water.

	Strip 1.	Strip 2.	Strip 3.	Strip 4.	Strip 5.	Strip 6.
	Pct.	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*
Uranyl Nitrate	100	80	60	40	20	0
Uranyl Sulphate	0	20	40	60	80	100

PLATE 79. *A*. Uranyl Acetate in Water. Depth of cell, 10 mm. Concentration of Uranyl Salt, 0.05 normal. Concentration Nitric Acid, 0.0028, 0.0056, 0.0140, 0.028, 0.140, 0.28, and 0.56 normal.

B. Uranyl Nitrate in Water to which Hydrochloric Acid is added.

PLATE 80. *A*. Uranous Acetate in Water to which Nitric Acid is added.

B. The first four strips give the effect of adding Hydrochloric Acid to a Nitric Acid solution of Uranyl Nitrate. The remaining strips represent the same effect obtained by using a greater depth of cell.

PLATE 81. *A*. Uranous and Aluminium Chlorides in Water to which Nitric Acid is added.

B. Uranyl Nitrate in Water to which Sulphuric Acid is added. Depth of cell 15 mm. Concentration of Uranyl Salt, 0.04 normal. Percentage of acid, 1.84, 3.68, 7.36, 14.72, 29.44, 58.88, and 88.32.

PLATE 82. *A*. Uranyl Nitrate to which Acetic Acid is added.

B. Uranyl Nitrate in Water to which Sulphuric Acid is added. Depth of cell 8 mm.; otherwise this is the same as *B*, Plate 81.

PLATE 83. *A*. Uranyl Nitrate in Water to which Sulphuric Acid is added.

B. Uranyl Nitrate in Water to which Acetic Acid is added.

PLATE 84. *A*. Uranous Chloride in Water. Concentration constant. Depth of cell, 1.2' 2, 4, 8, 16, and 32 mm.

B. Uranous and Aluminium Chlorides in Water. Depth of cell, 1.2, 2, 4, 8, 16, and 32 mm.

PLATE 85. *A*. This spectrogram shows the absorption of Uranous Chloride in Acetone to which more and more Water is added. The "Water" and "Acetone" bands appear on this plate.

B. This spectrogram shows the same process, a more concentrated solution of Uranous Chloride in Acetone being used in this case.

PLATE 86. *A*. Uranous Chloride in Glycerol and mixtures of Glycerol and Water. The first strip represents the absorption of a 6 mm. solution of Uranous Chloride in Glycerol. Succeeding strips show the effect of the addition of Water.

B. This is exactly similar to *A* except that Methyl Alcohol was added instead of Water.

PLATE 87. *A*. Uranous Chloride in Methyl Alcohol. Concentration constant.

B. Uranous Acetate in Methyl Alcohol. Concentration constant.

C. Uranous Chloride in Glycerol. Concentration constant. Depth of cell, 3, 4, 6, 9, 13, 18, and 24 mm.

PLATE 88. *A*. Uranous Chloride in Ethyl Alcohol. Concentration constant. Depth of cell, 3, 6, 12, 24, and 35 mm.

B. Uranous Chloride in Methyl Alcohol. Concentration constant. Depth of cell, 3, 6, 12, 24, and 35 mm.

PLATE 89. *A*. Uranyl Chloride in Methyl Alcohol to which Water is added.

B. Uranous Chloride in Methyl Alcohol. Concentration constant.

PLATE 90. *A*. Uranous Chloride in Acetone. Depths of cell, 5, 6, 8.3, and 15 mm. The first strip represents Uranous Chloride in Acetone, and the following strips represent the same to which Hydrochloric Acid had been added.

B. In this case Uranyl Chloride instead of Uranous Chloride was used. Depth of cell, 2, 3.4, 4, 5, 11, and 30 mm.

C. Strips 1, 2, and 3 represent the same effect as *A*.

Strip 4 represents an Ether solution of Uranous Chloride.

Strips 5, 6, and 7 the absorption of 2, 5, and 14 mm., respectively, of Uranous Chloride in Acetone.

PLATE 91. *A*. Uranous Bromide in Methyl Alcohol.

B. Uranous Acetate in Water to which more and more Nitric Acid is added.

PLATE 92. *A*. Uranous Bromide in Water, Beer's law test. The original solution consisted of an 0.8 mm. layer. To this was added Water so as to make the depth of solution 2.8, 6, 12.5, 22, and 35 mm.

B. Uranous Bromide in Glycerol. 0.06 normal Concentration. Depth of cell, 5, 7.5, 10, 15, 20, 26, and 33 mm.

PLATE 93. *A*. Uranyl Nitrate in Nitric Acid to which Sulphuric Acid is added. Depth of cell, 8, 8.4, 9, 12, and 17 mm.

B. Uranous Acetate in Acetic Acid to which Hydrobromic Acid is added. Depth of cell, 22, 22.3, 24, 30, and 36 mm.

PLATE 94. *A*. An Acid Solution of Uranous Chloride to which Ethyl Alcohol is added. Depth of cell being 4.5, 5, 7, 15, and 35 mm.

B. Uranous Chloride in Water to which Acetic Acid is added. Depth of cell, 5, 5.8, 7.5, and 26 mm.

PLATE 95. *A*. Uranous Chloride in Acetone. Depth of cell varied.

B. Uranous Chloride in Methyl Alcohol. Depth of cell, 2.4, 6, 8, and 12 mm.

C. Uranous Chloride in Glycerol. Depth of cell, 2, 4, 6, 8, 12, and 24 mm.

PLATE 96. *A*. Uranous Chloride in Water to which Ethyl Alcohol is added. Depth of cell, 3.2, 4.4, 6.4, 12, and 22.5 mm.

B. Uranous Acetate in Water. Depth of cell, 3, 6, 12, 24, and 35 mm.

C. Uranyl Acetate in Acetone and Acetic Acid. Depth of cell 3, 6, 12, 24, and 35 mm.

PLATE 97. *A*. Uranous Acetate in Water to which Nitric Acid is added.

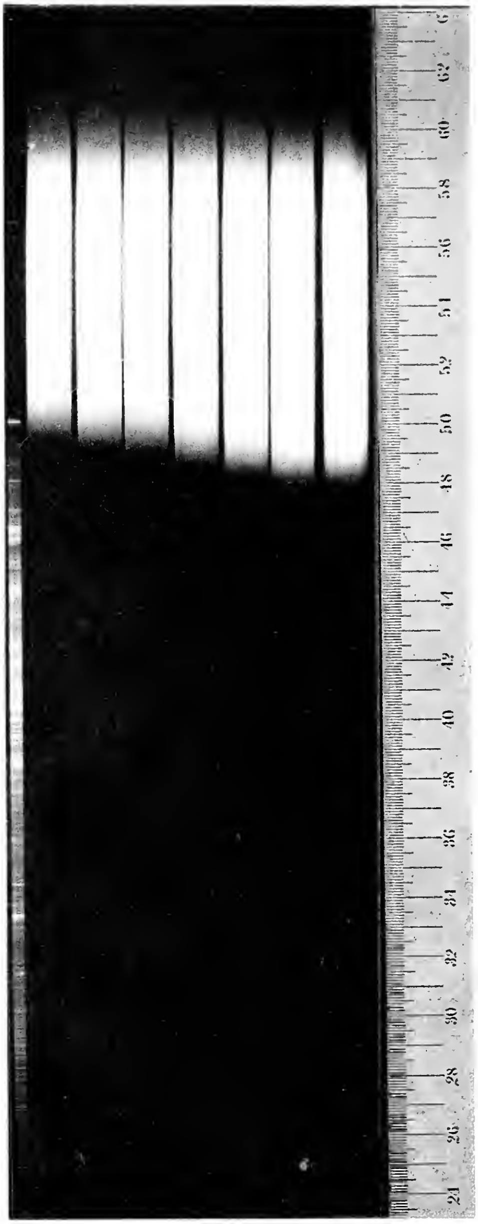
B. Uranyl Nitrate in Strong Nitric Acid. Strip 1, 1.2 mm. of solution then 2, 3, 5, and 12 (4 mm.) drops of Hydrochloric Acid was added. The last strip shows the absorption of 9.5 mm. of the solution.

PLATE 98. *A*. Uranous Chloride to which a concentrated solution of Aluminium Chloride is added. Strip 1, 3 mm. of Uranous Chloride solution plus 1 mm. $AlCl_3$; strip 2, the same to which 2 mm. of $AlCl_3$ solution is added; strip 3, to which 10 mm. more of $AlCl_3$ is added; strip 4 is a 3 mm. solution of Uranous Chloride, and strip 5 is the same to which 13 mm. HCl has been added.

B. (1) Uranous Chloride in Water, 4 mm.; (2) plus Methyl Alcohol to 6.3 mm.; (3) plus Methyl Alcohol to 7.5 mm.; (4) Uranous Chloride in Water, 4 mm.; (5) the same plus Acetic Acid to 28 mm.; (6) 4 mm. of Uranous Chloride in Water plus 2 mm. HNO_3; (7) 4 mm. Uranous Chloride in Water plus 19 mm. H_2SO_4.

INDEX.

PLATE 1



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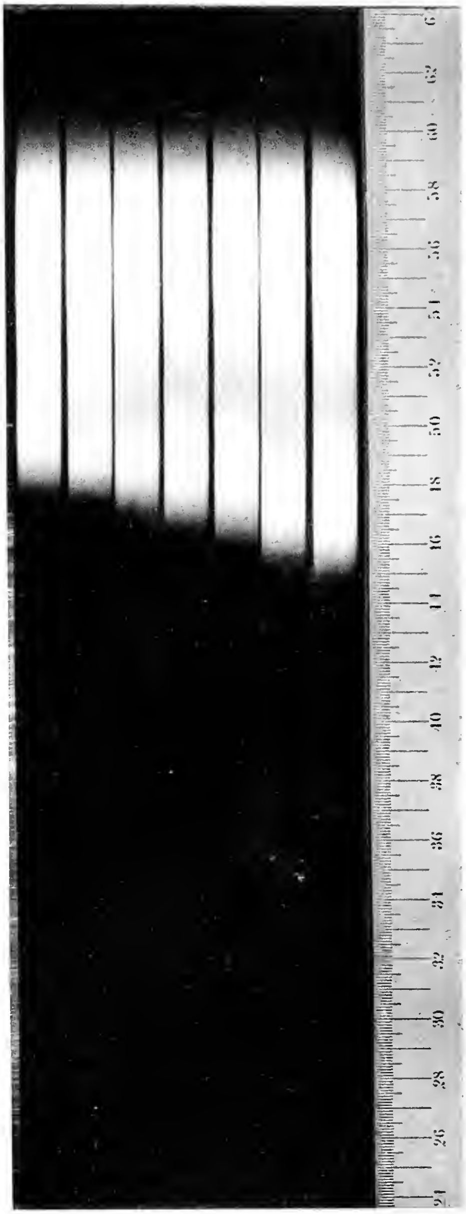

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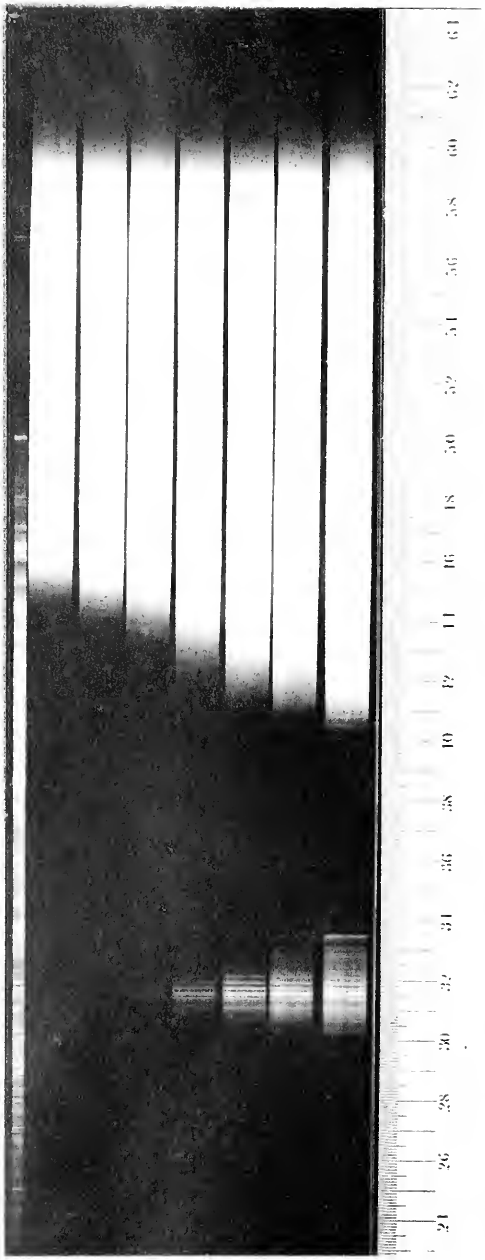

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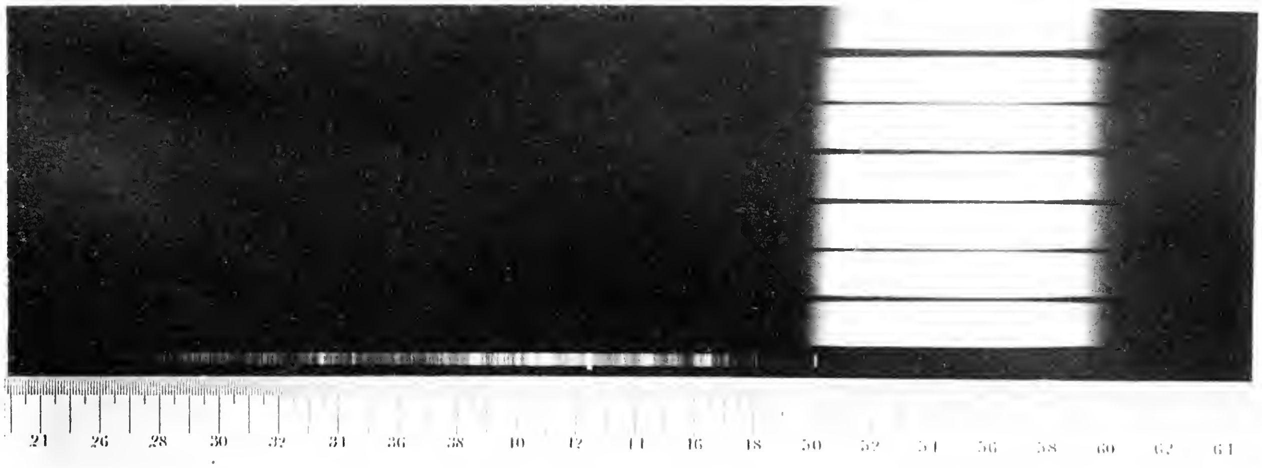
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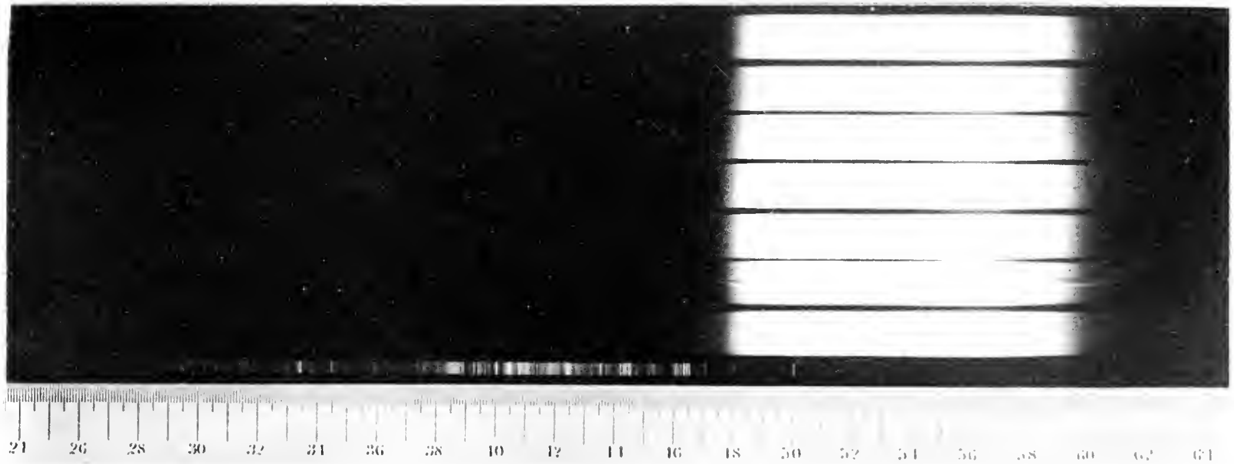
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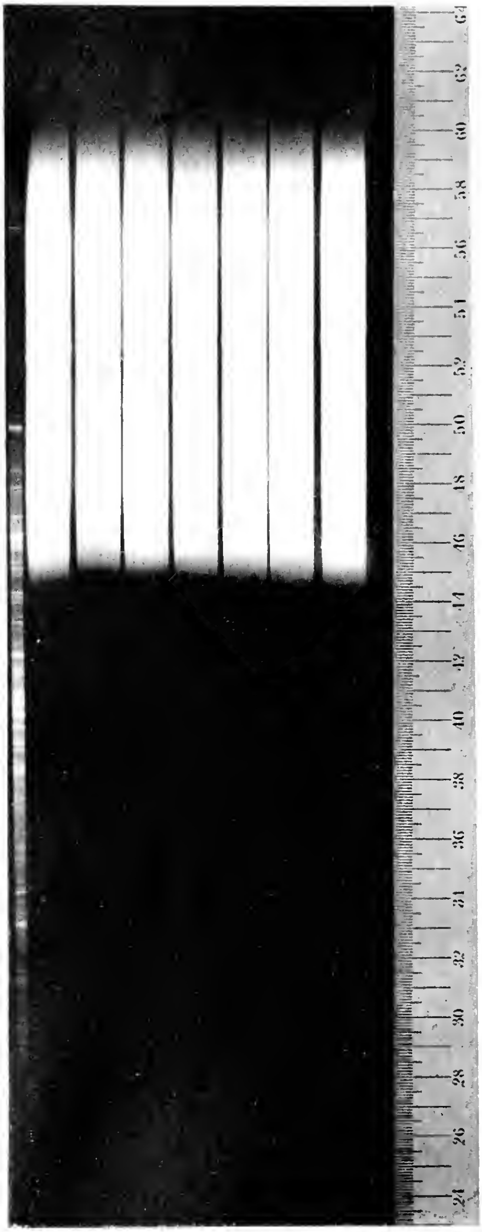
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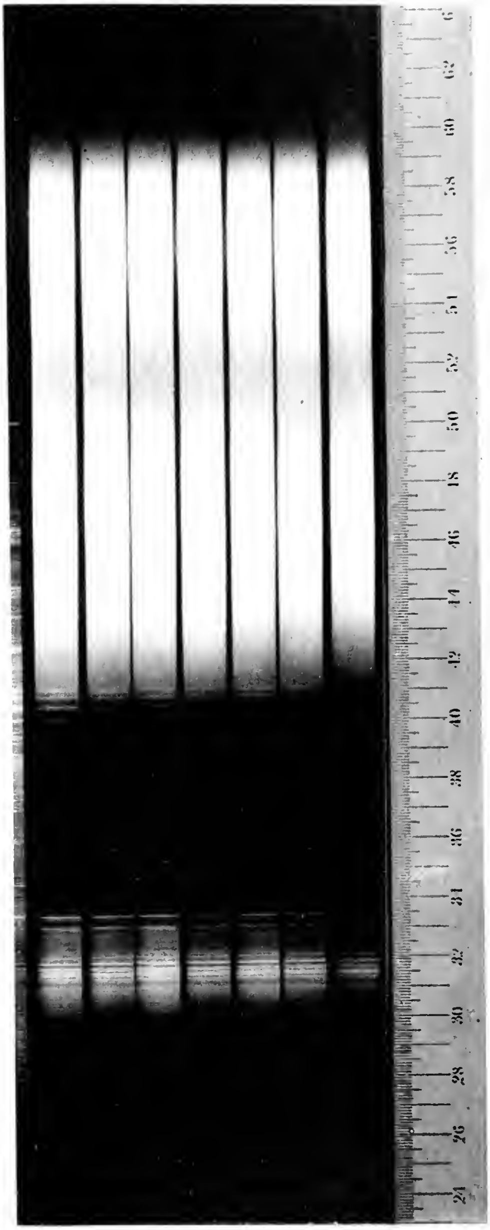
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PLATE 5

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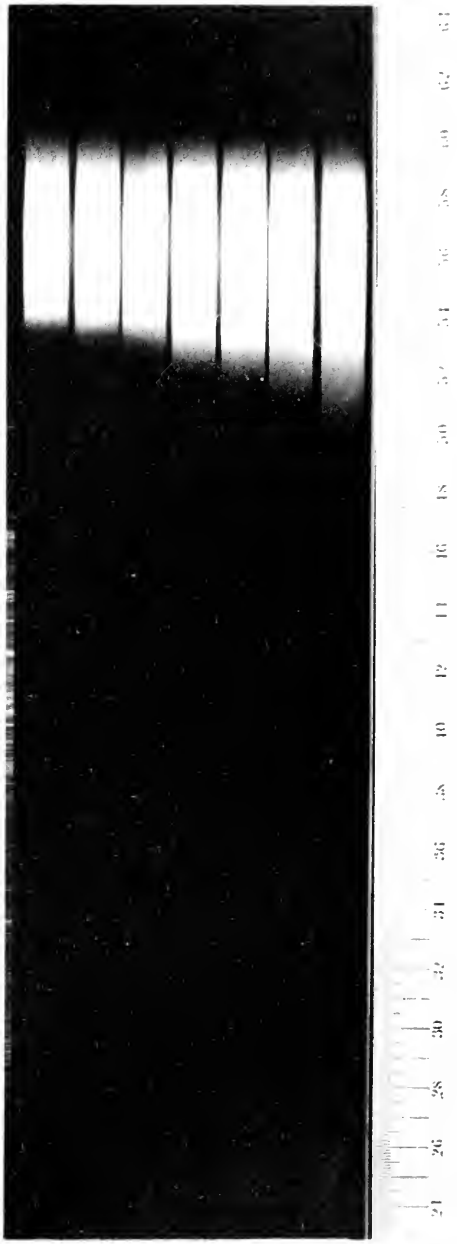

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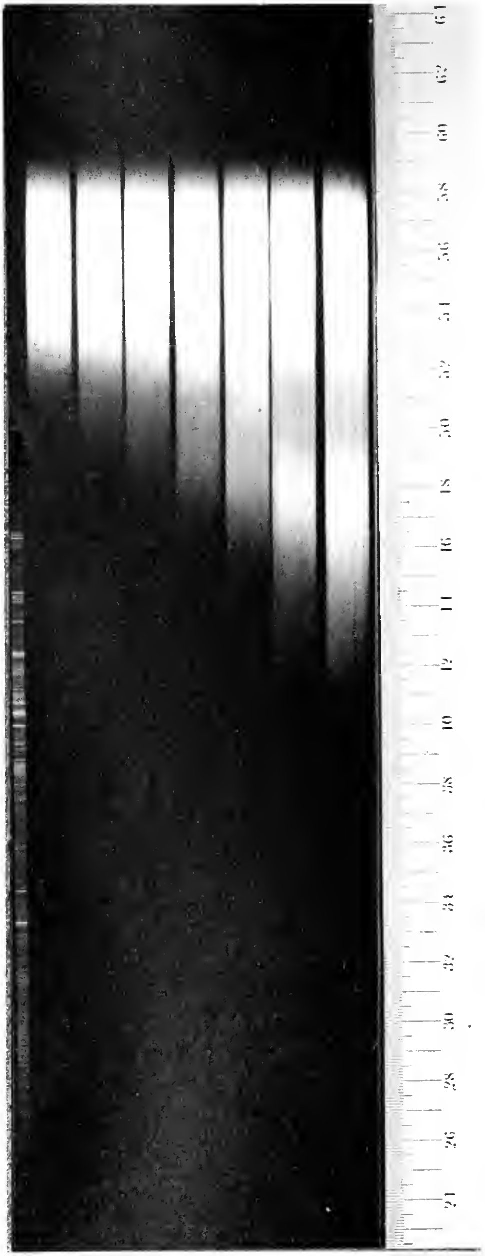

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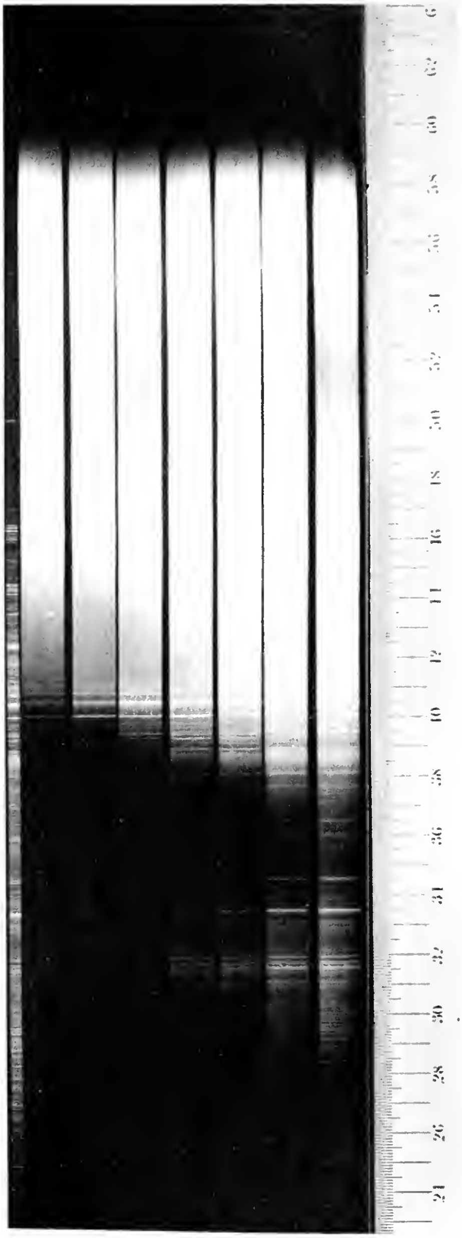

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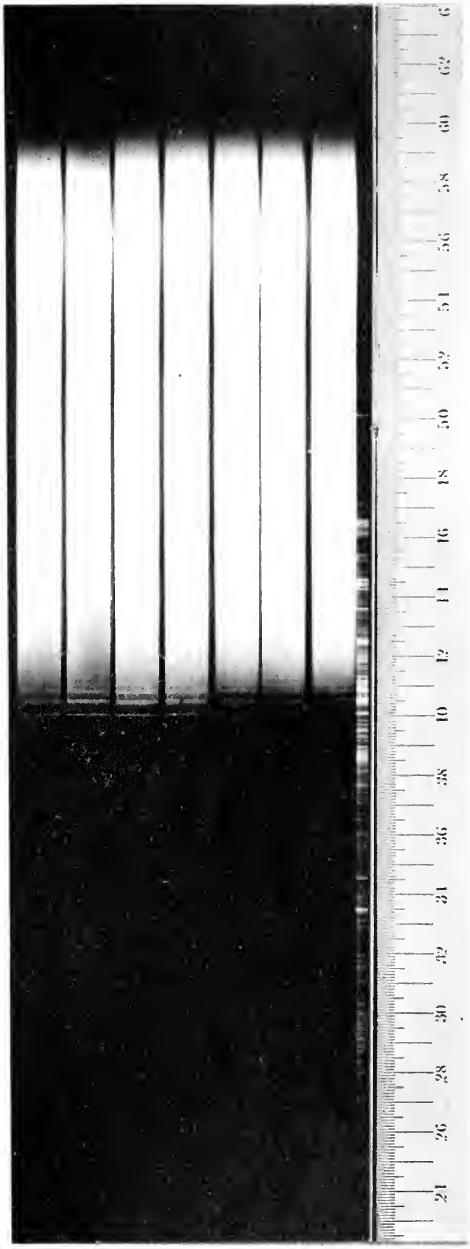

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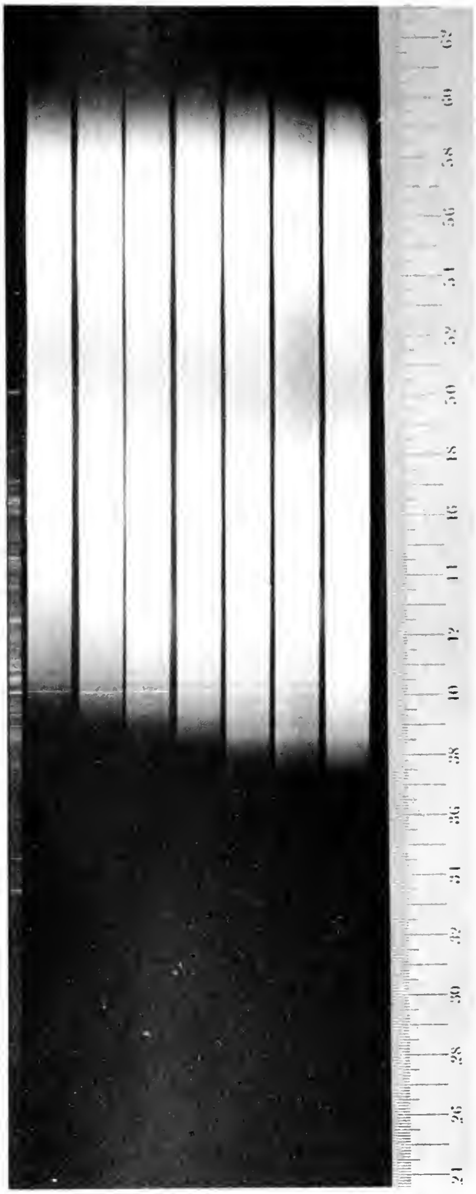

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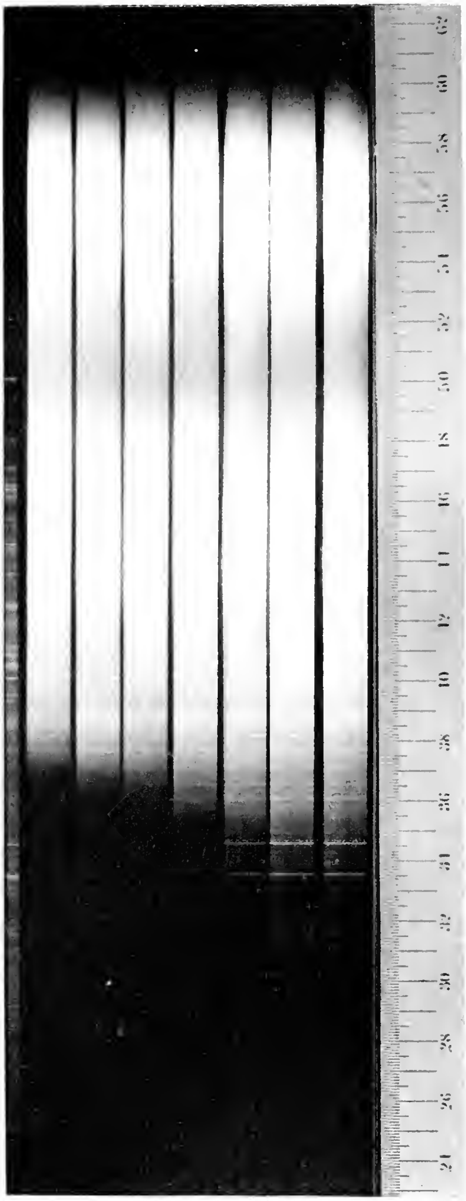

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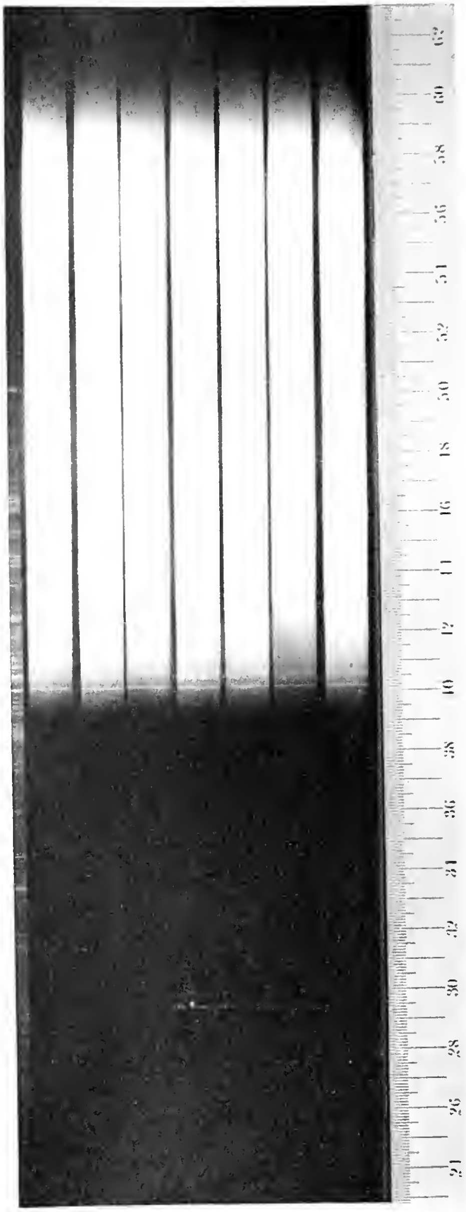

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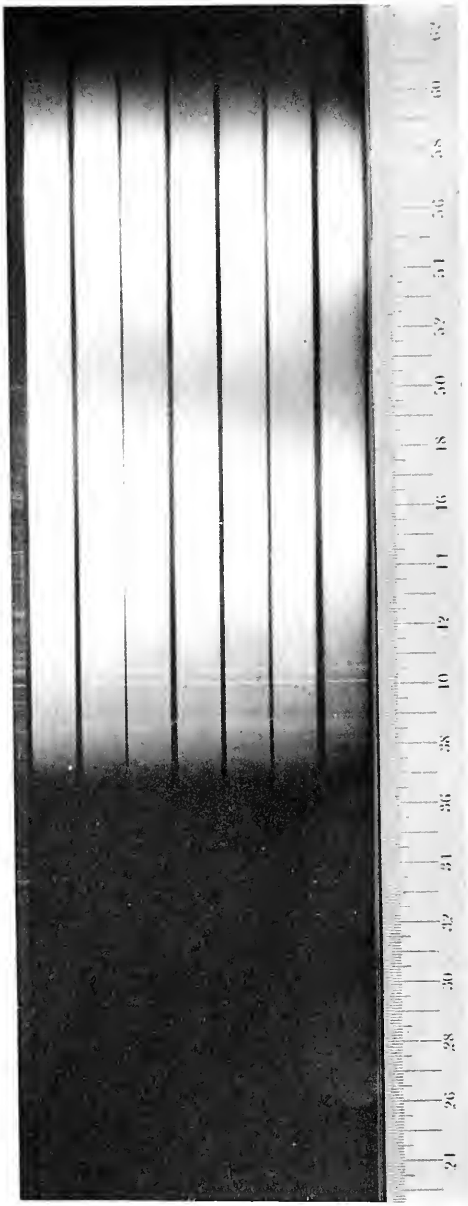

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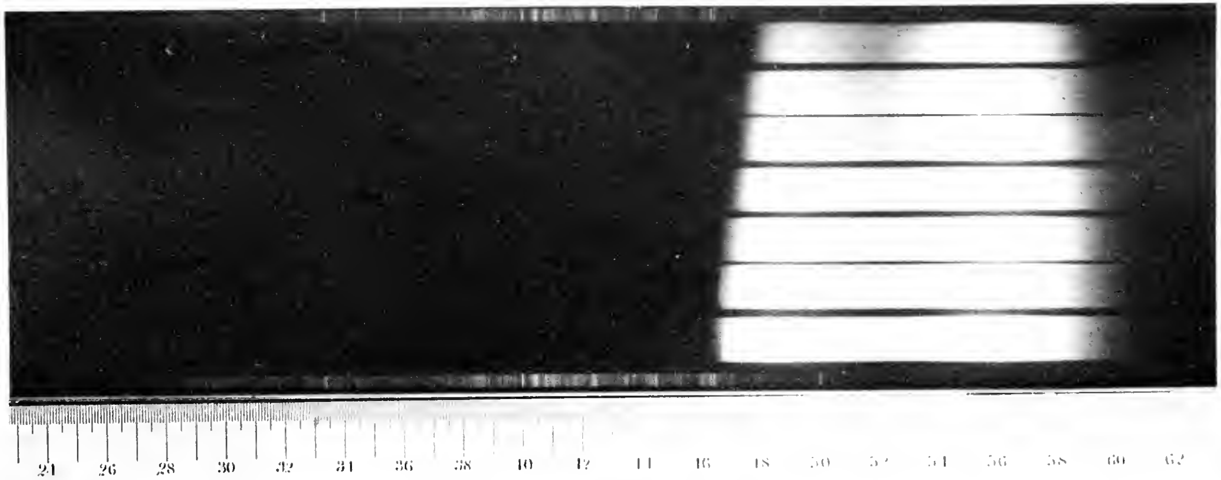
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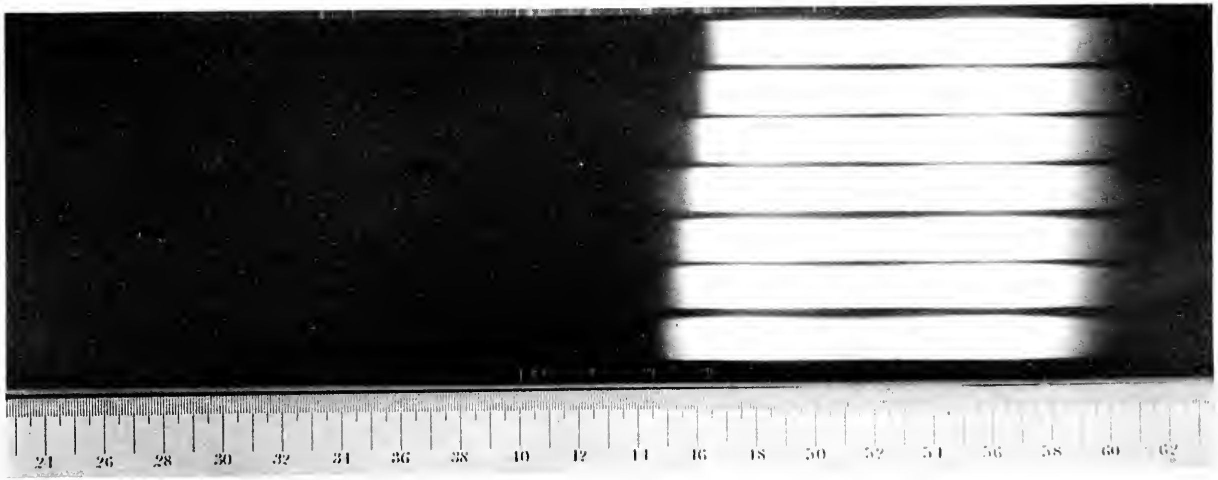
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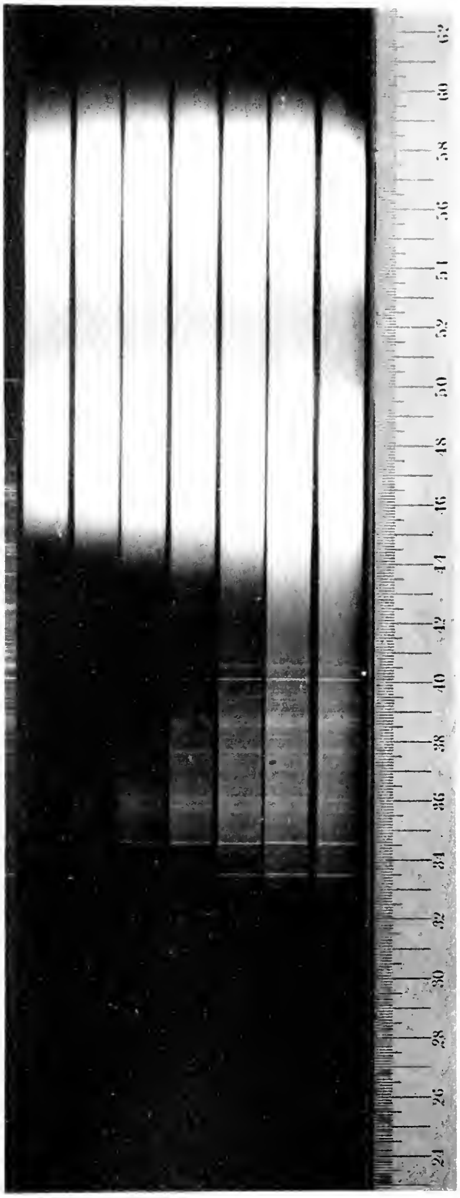
PLATE 11



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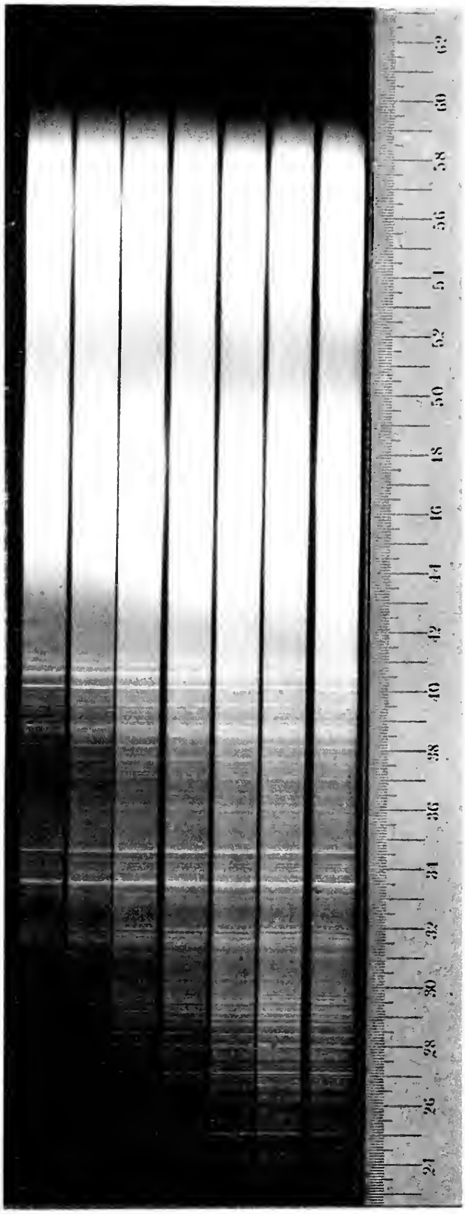

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PLATE 12

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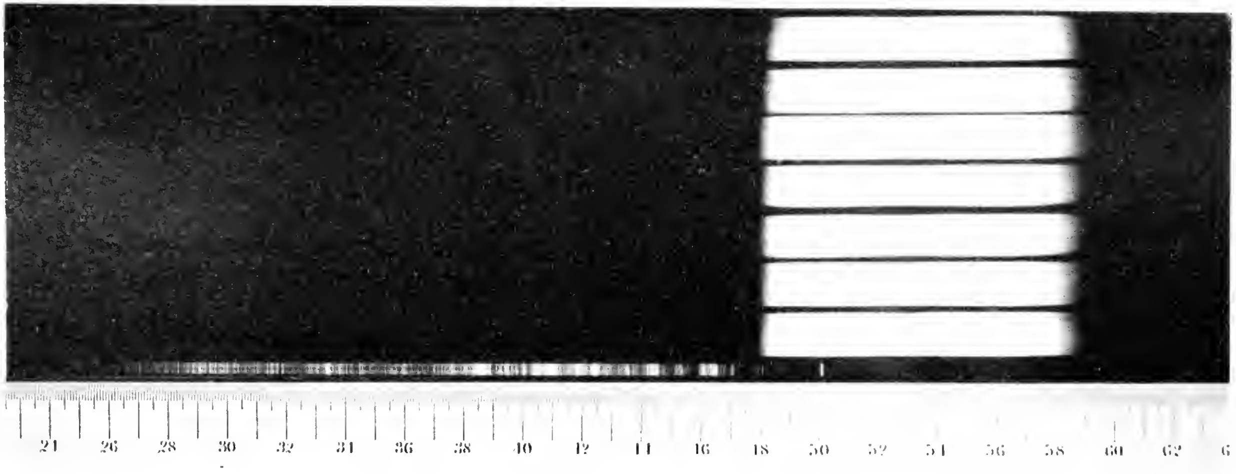

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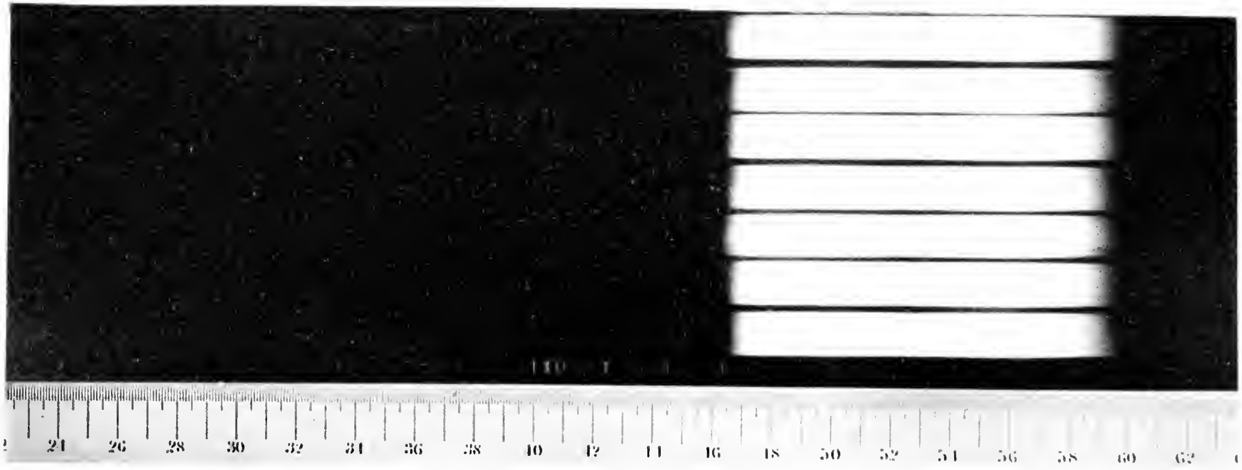

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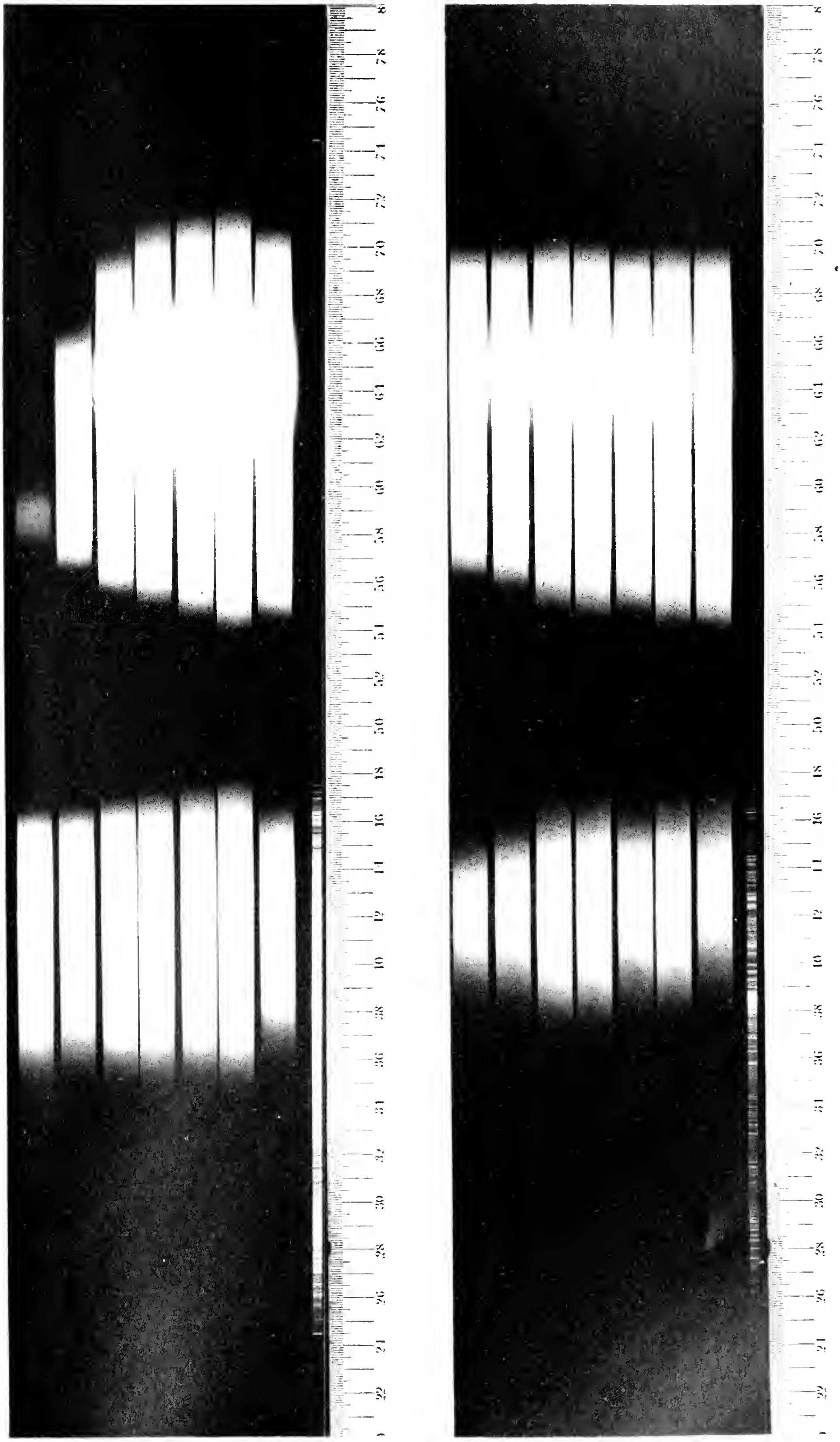
PLATE 13



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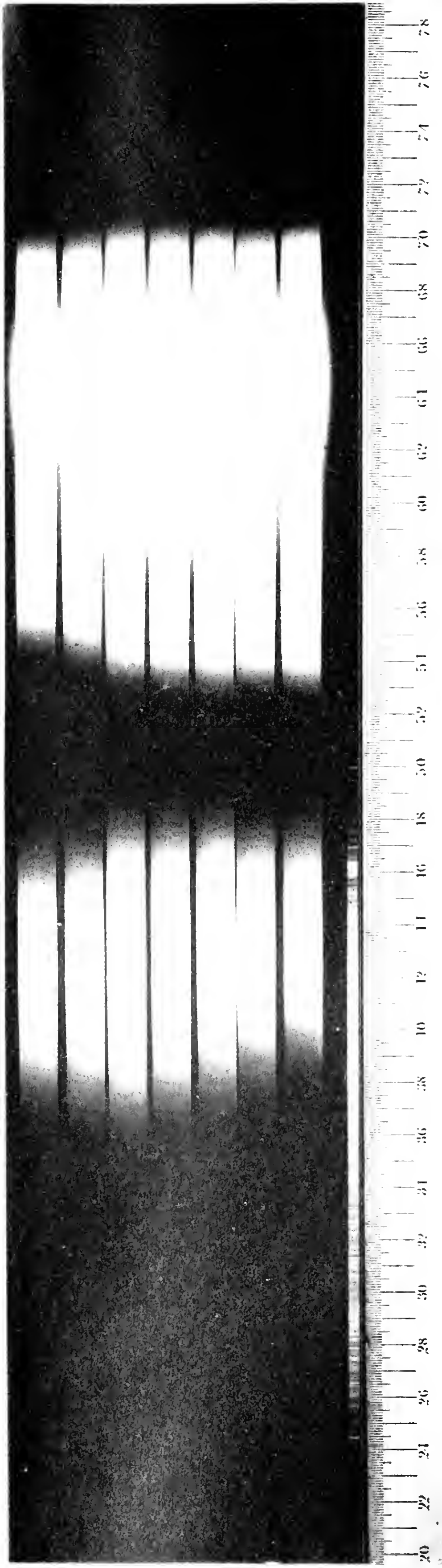

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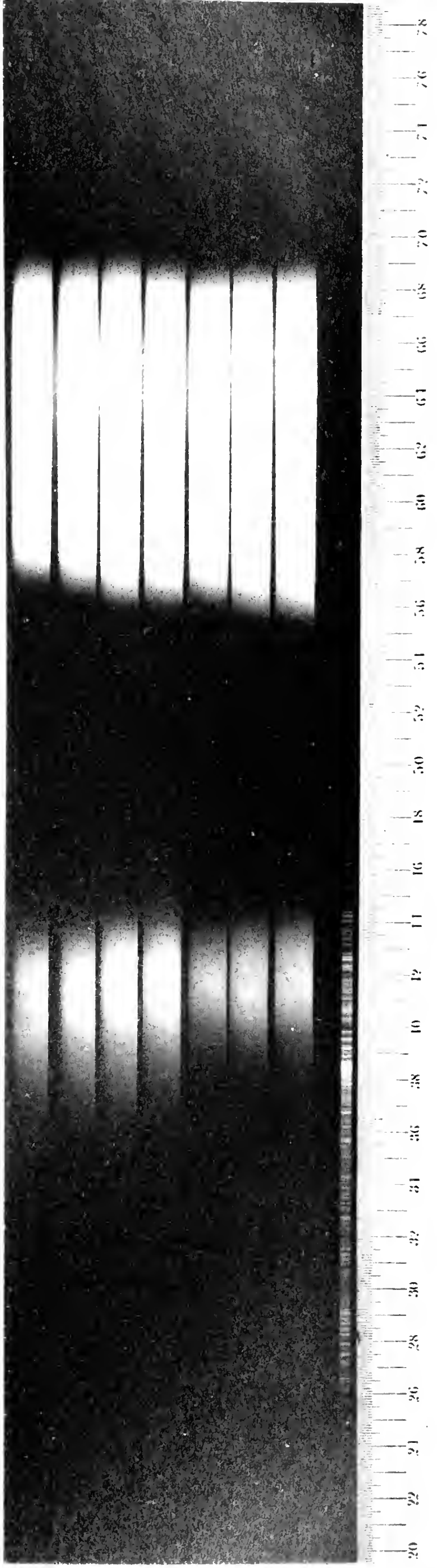

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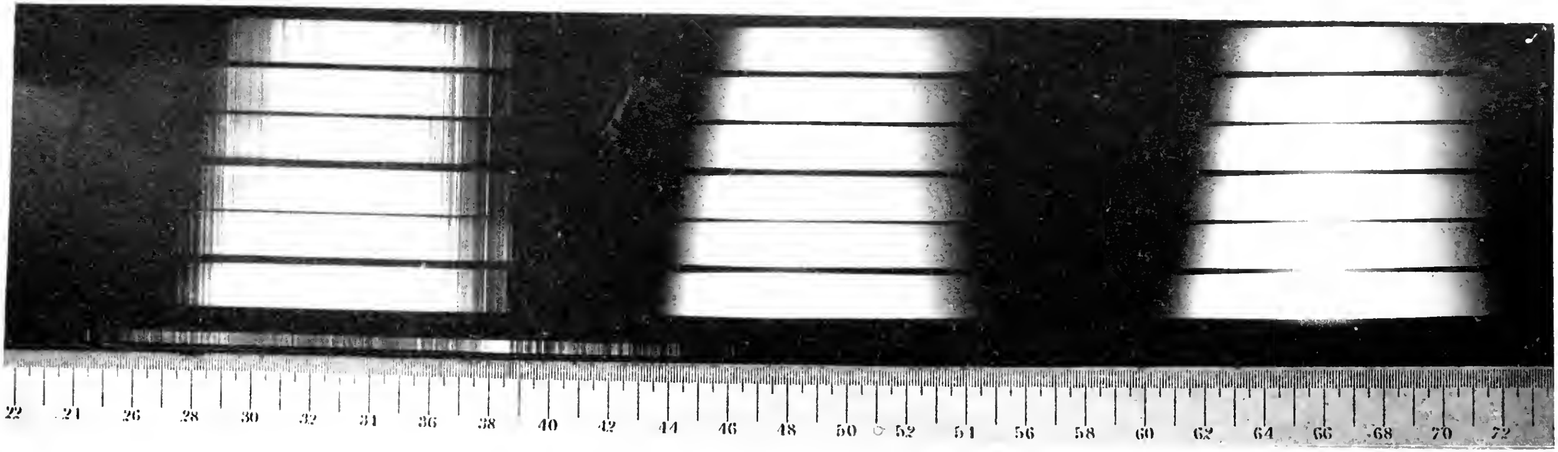

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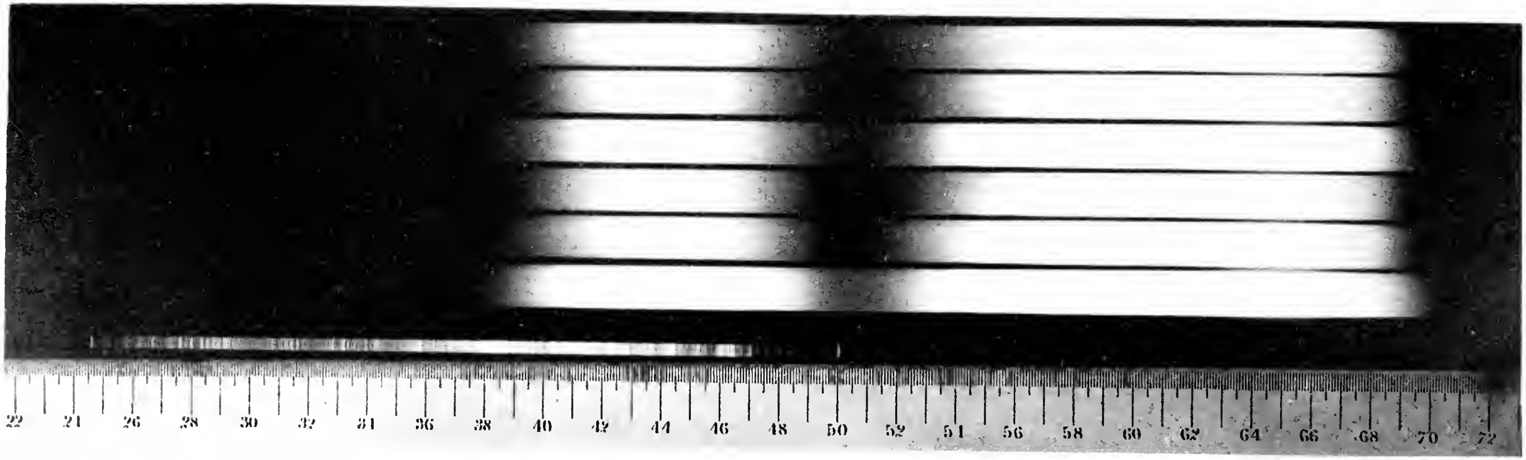

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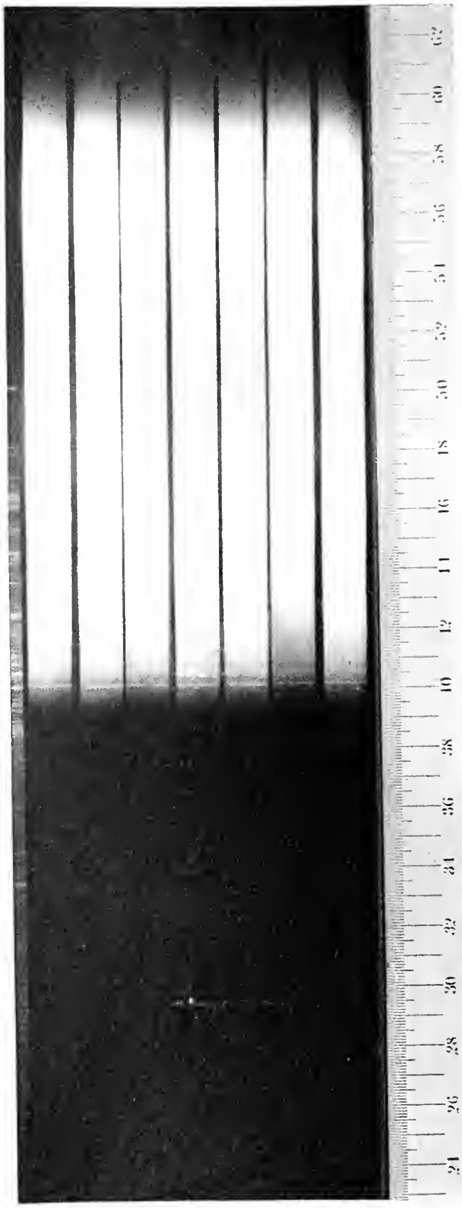
CAMPBELL ART CO., ELIZABETH, N. J.

PLATE 9



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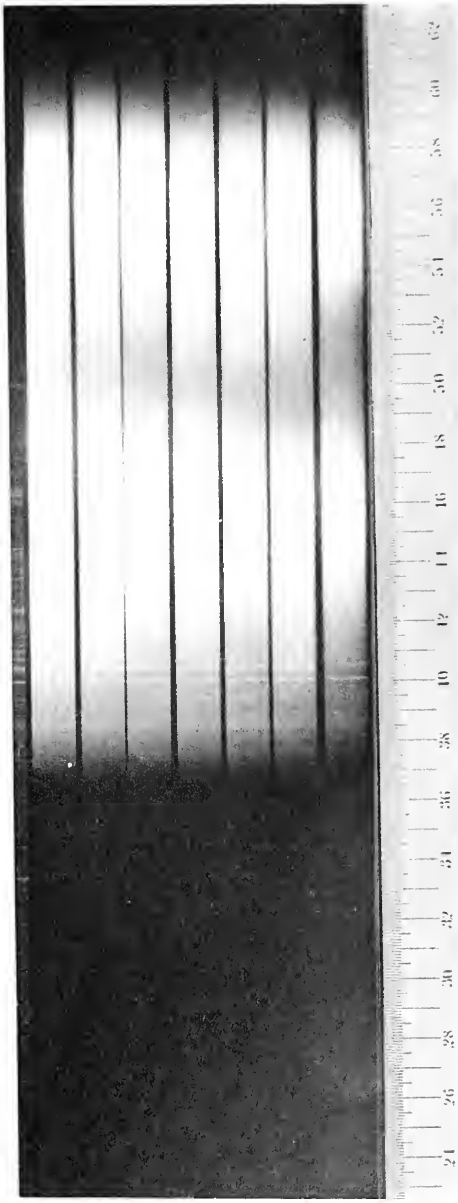

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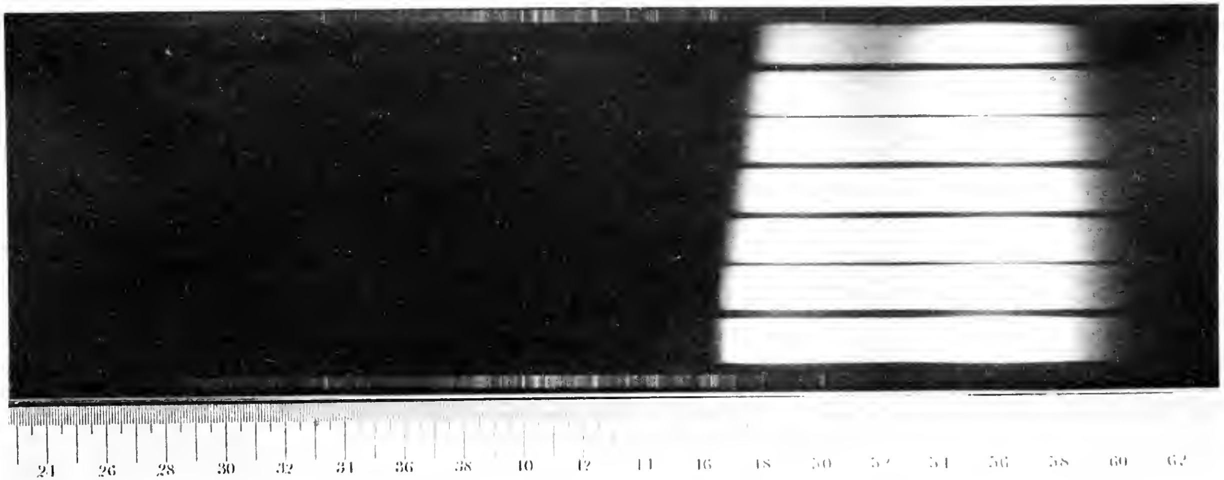
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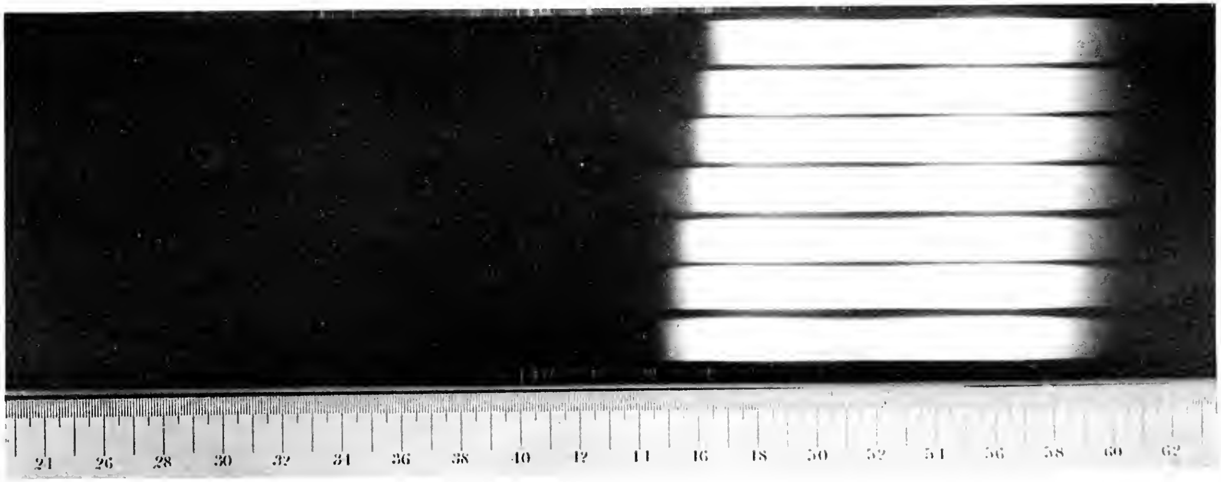
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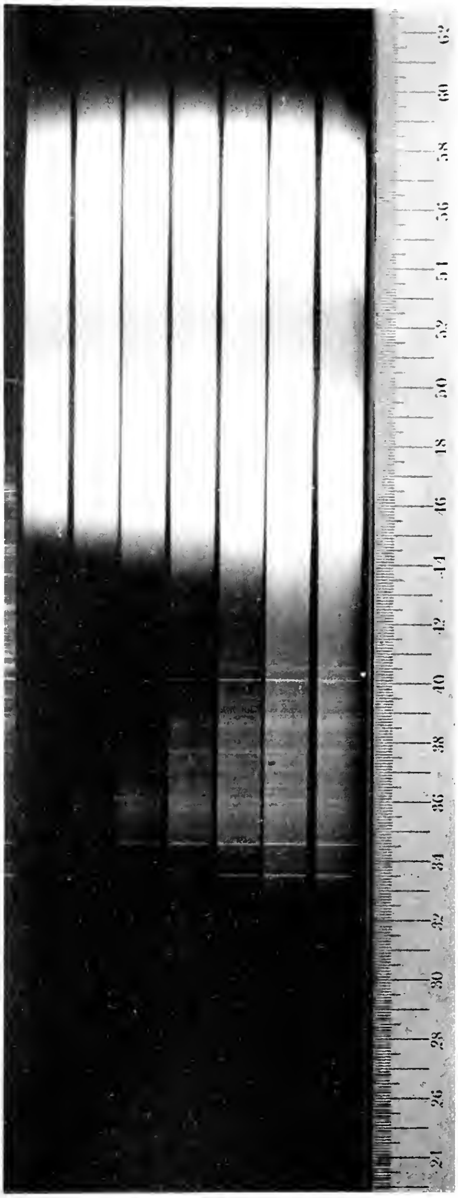
PLATE 11



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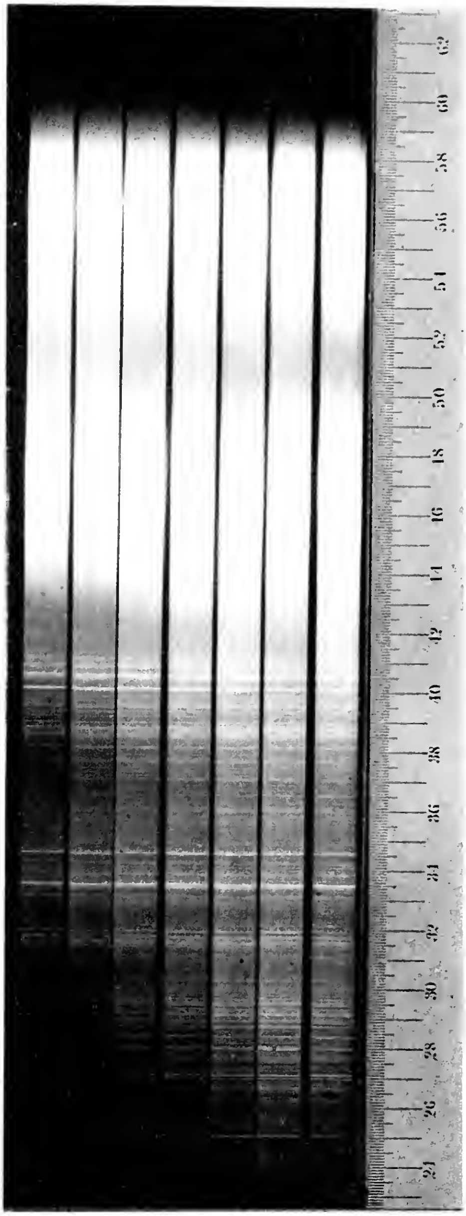

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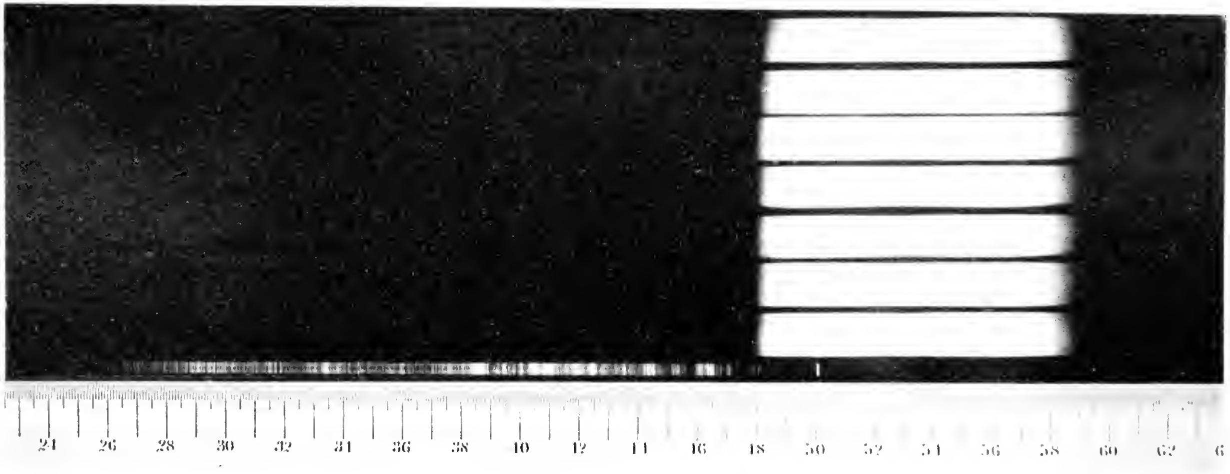
CAMPBELL ART CO., ELIZABETH, N



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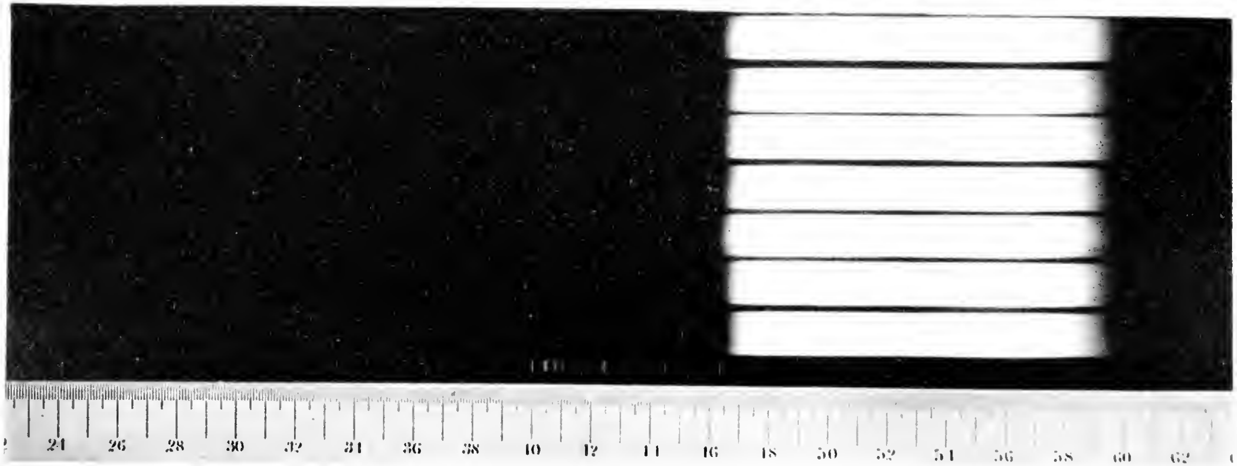

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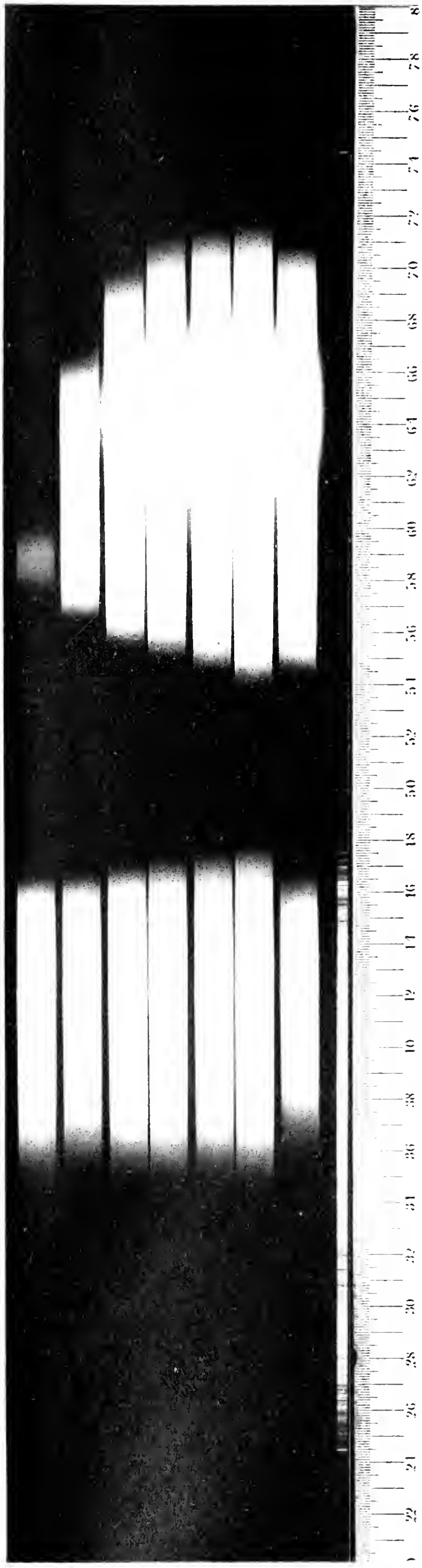
CAMPBELL ART CO., ELIZABETH, N. J.



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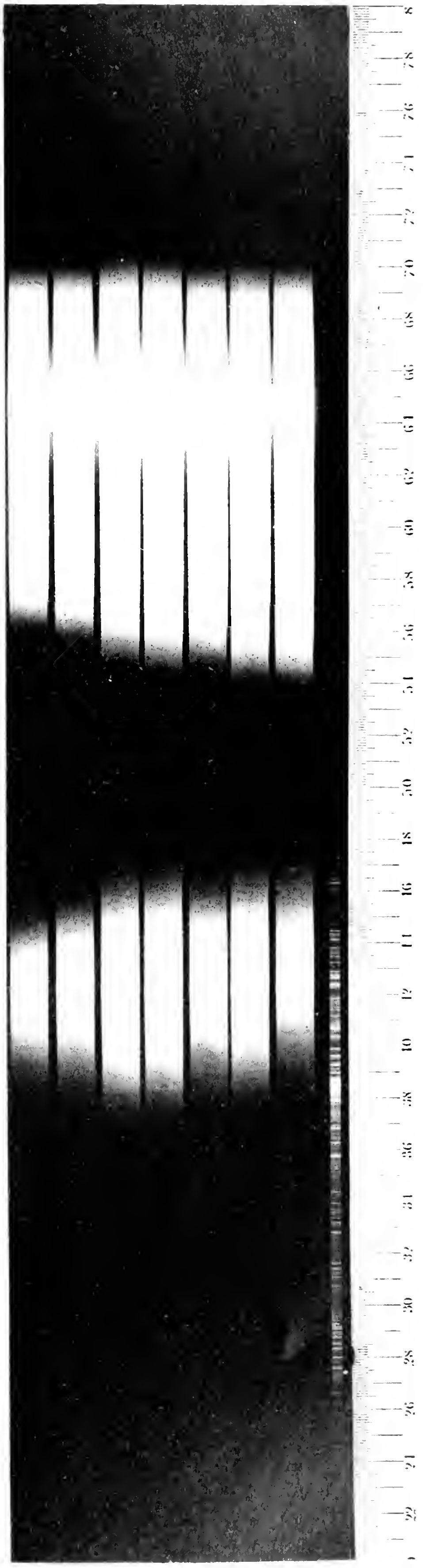

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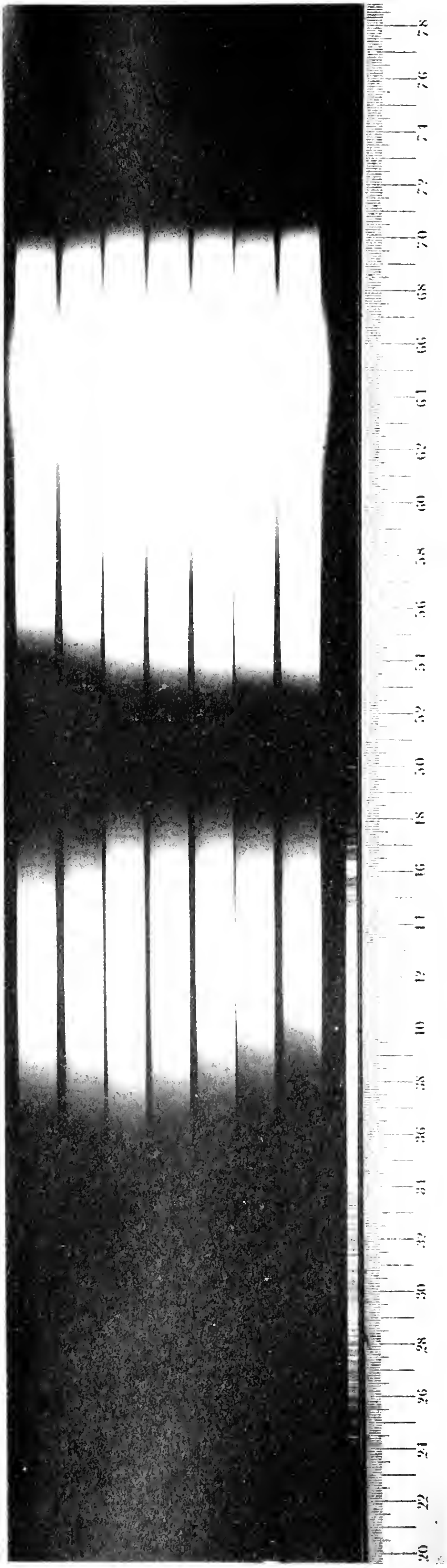
CAMPBELL ART CO., ELIZABETH, N. J



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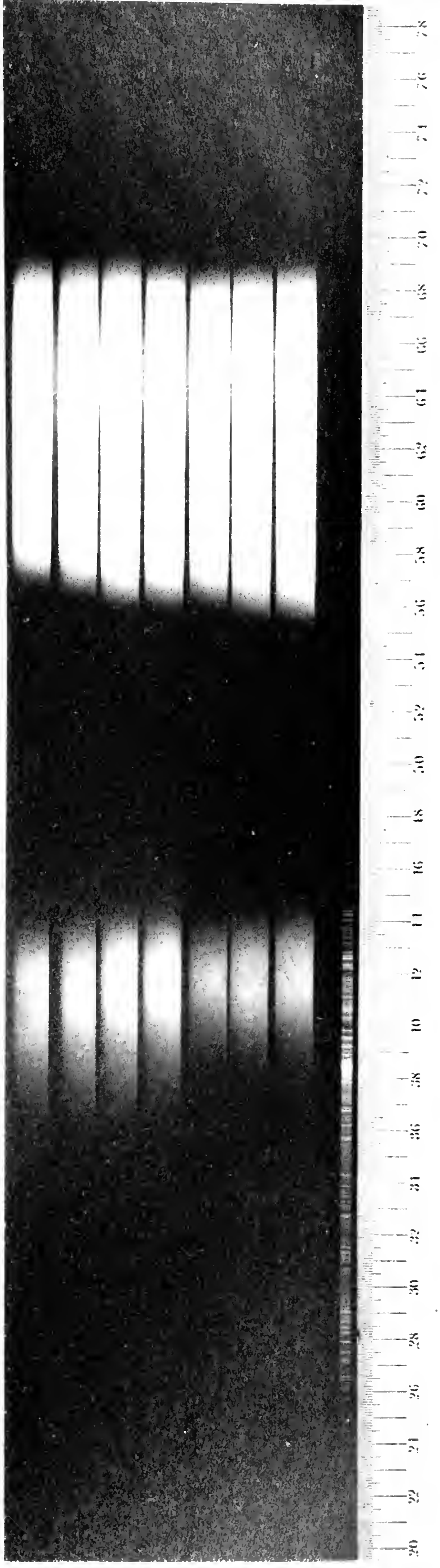

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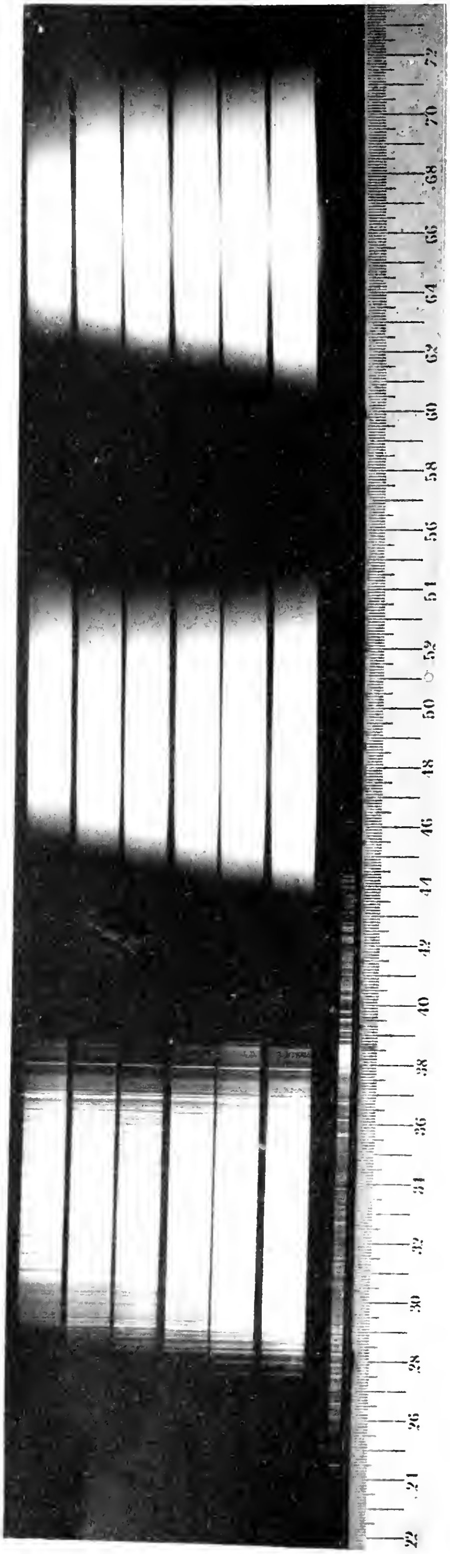
CAMPBELL ART CO., ELIZABETH, N. J



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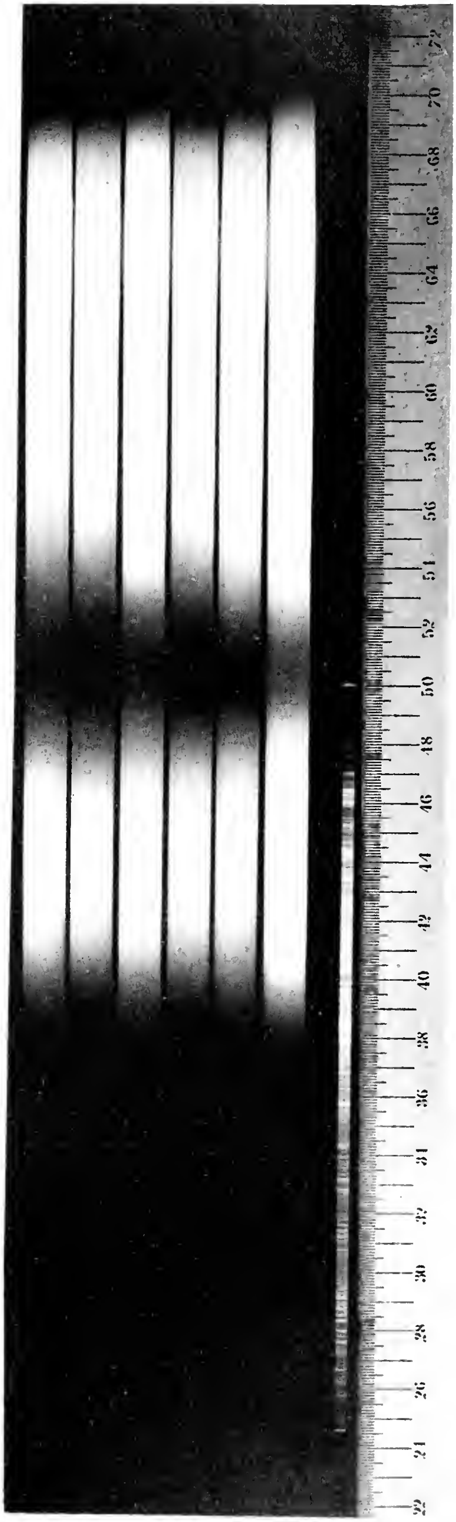

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CAMPBELL ART CO., ELIZABETH, N. J.


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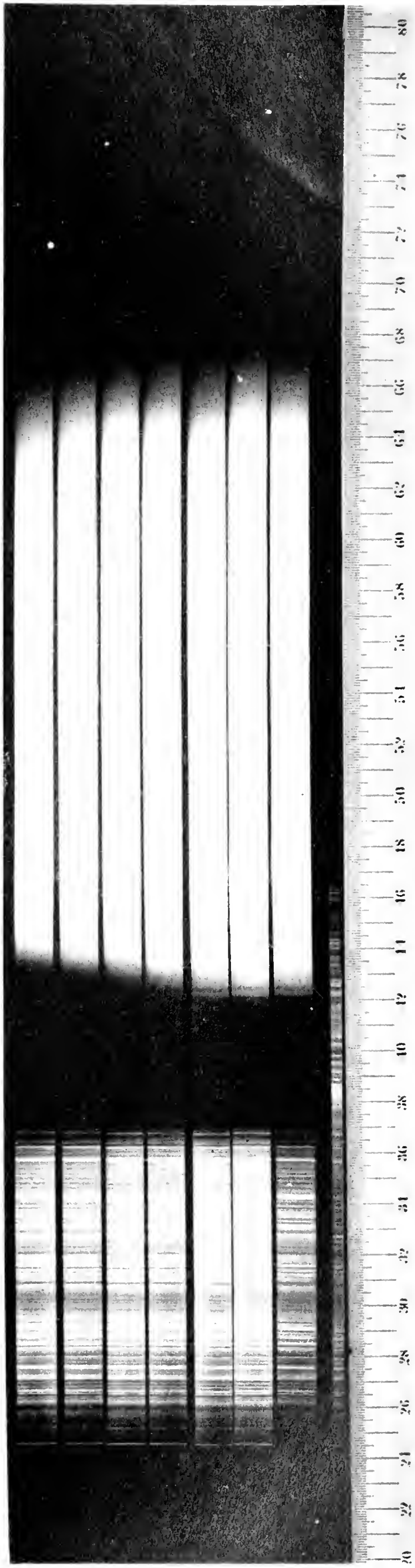
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PLATE 17

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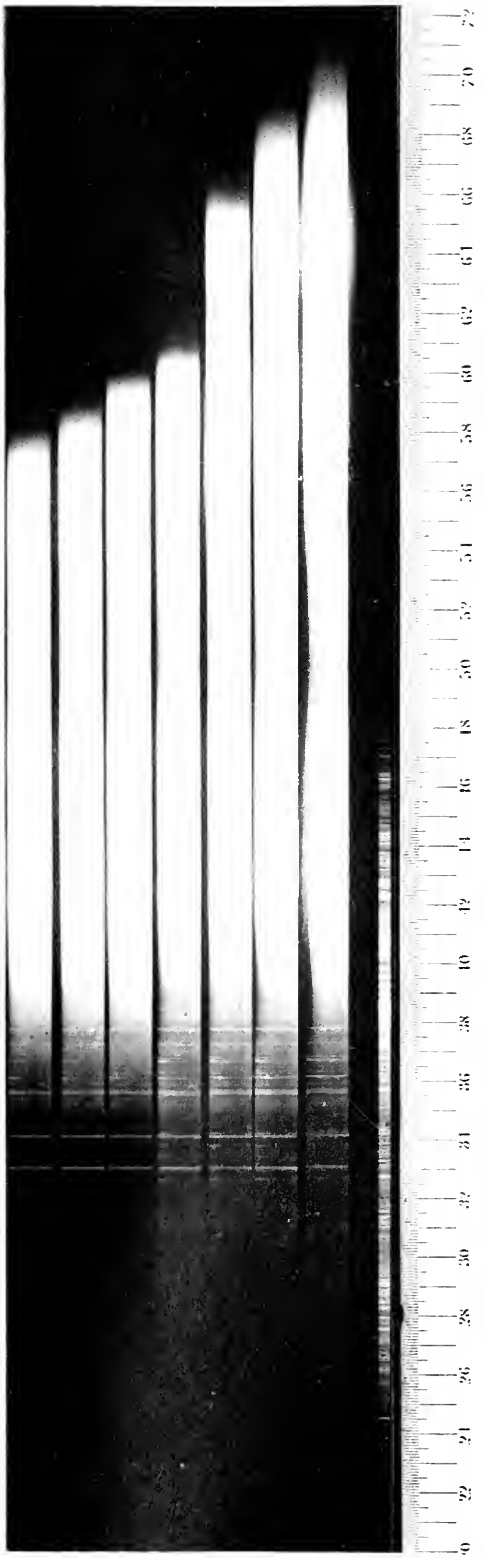
CAMPBELL ART CO., ELIZABETH N. J.



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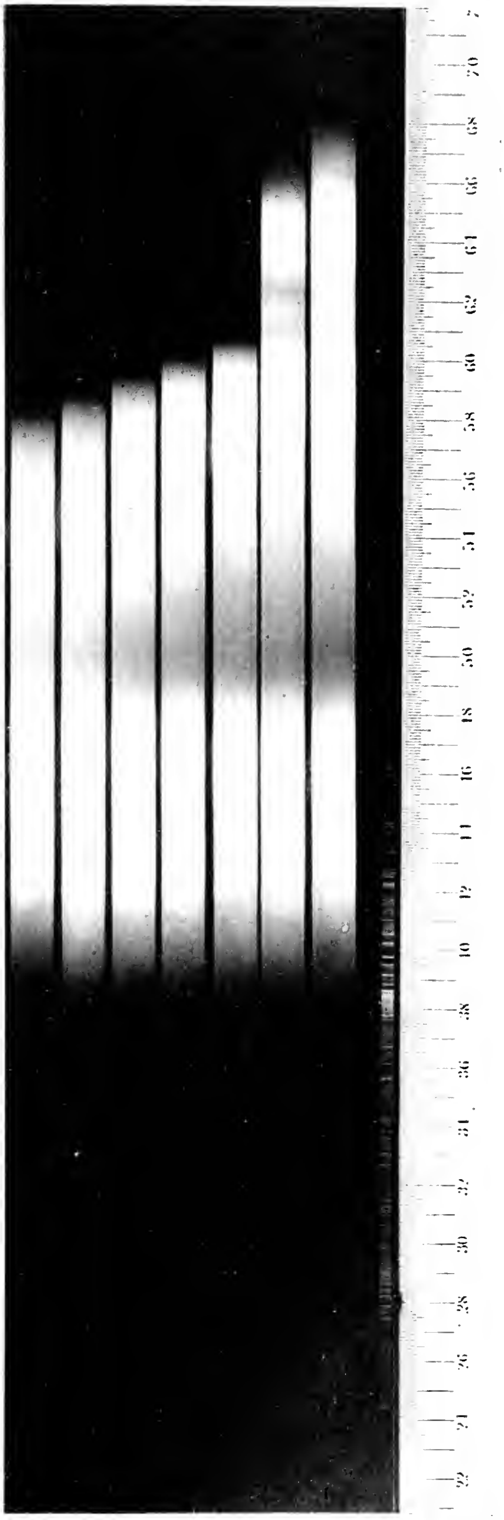

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CAMPBELL ART CO., ELIZABETH, N


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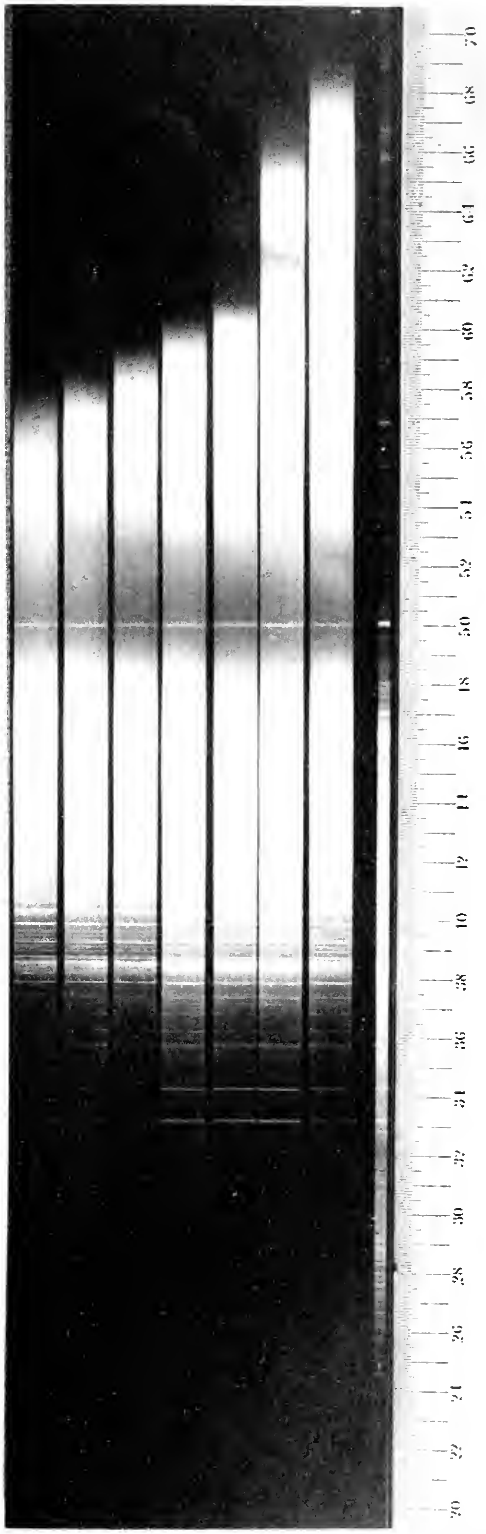
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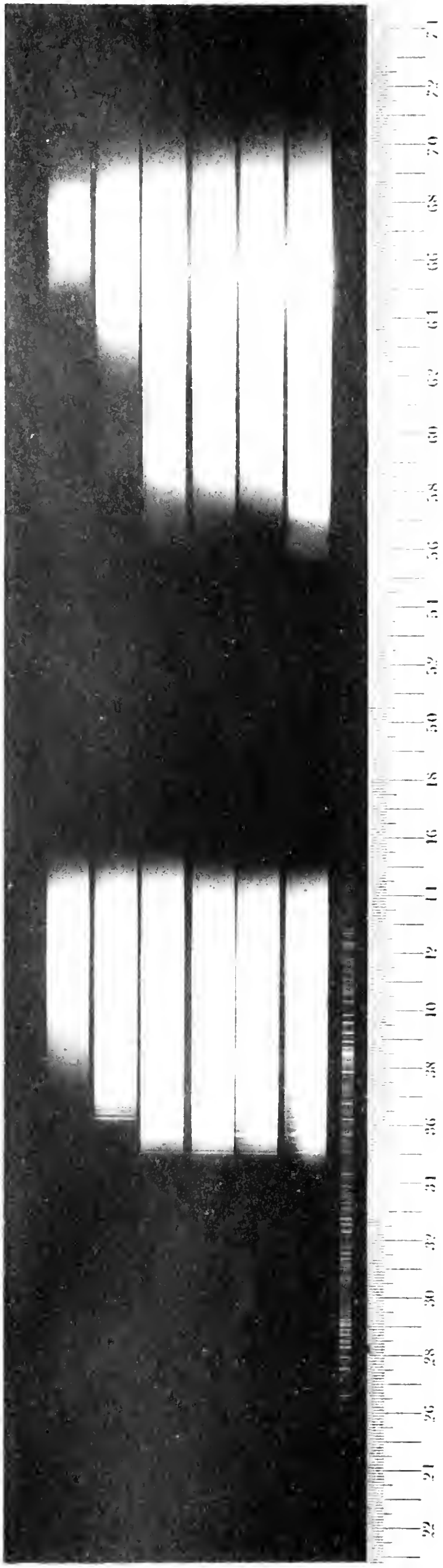

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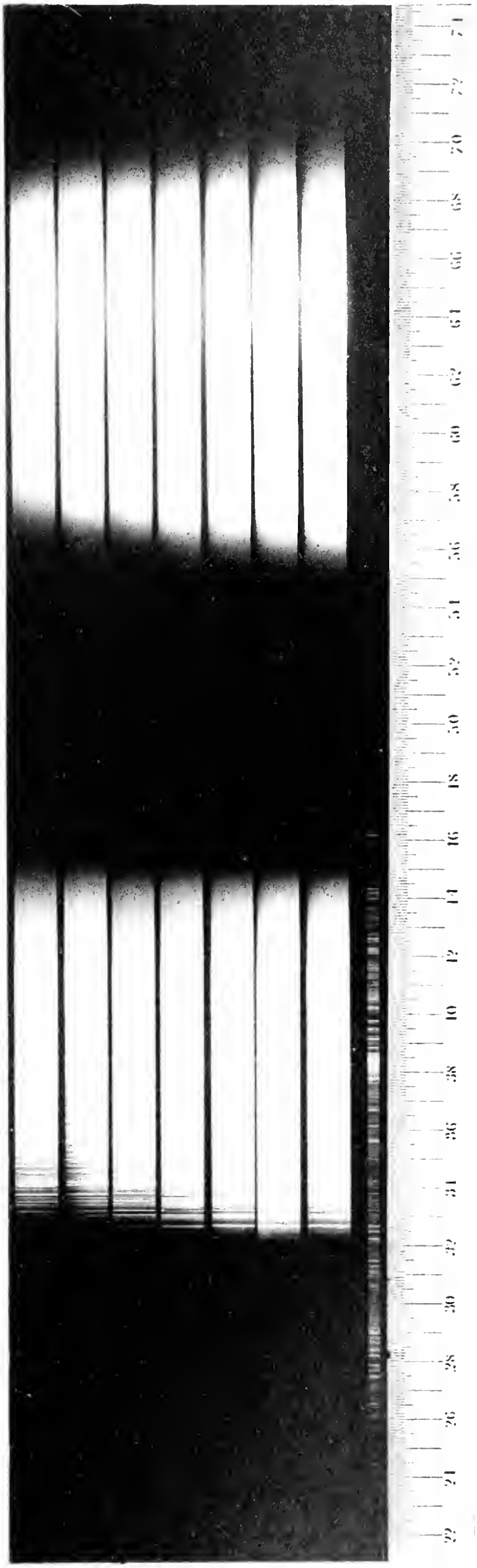

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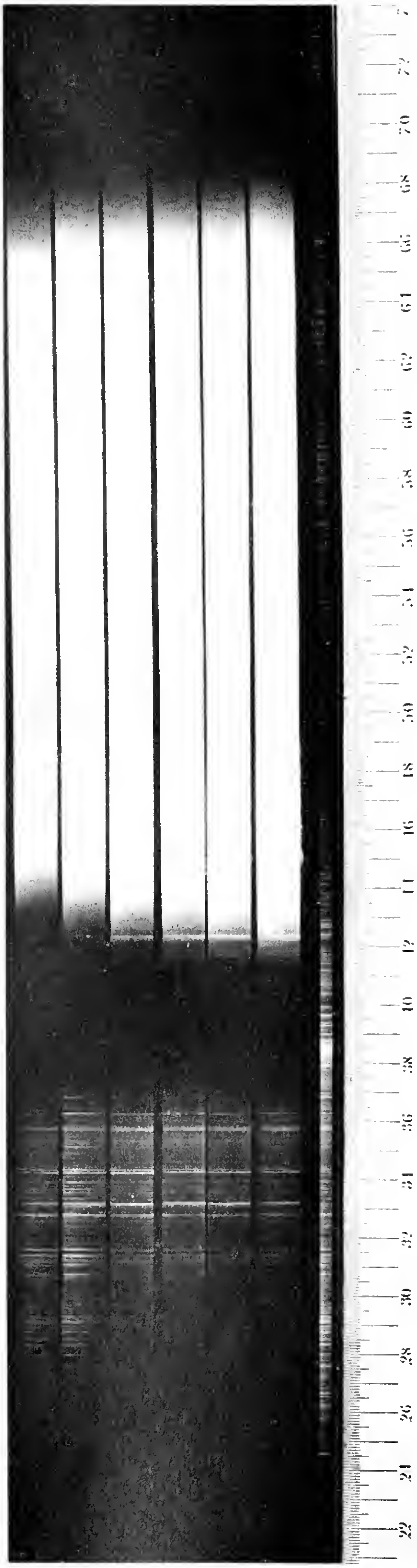

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CAMPBELL ART CO., ELIZABETH, N

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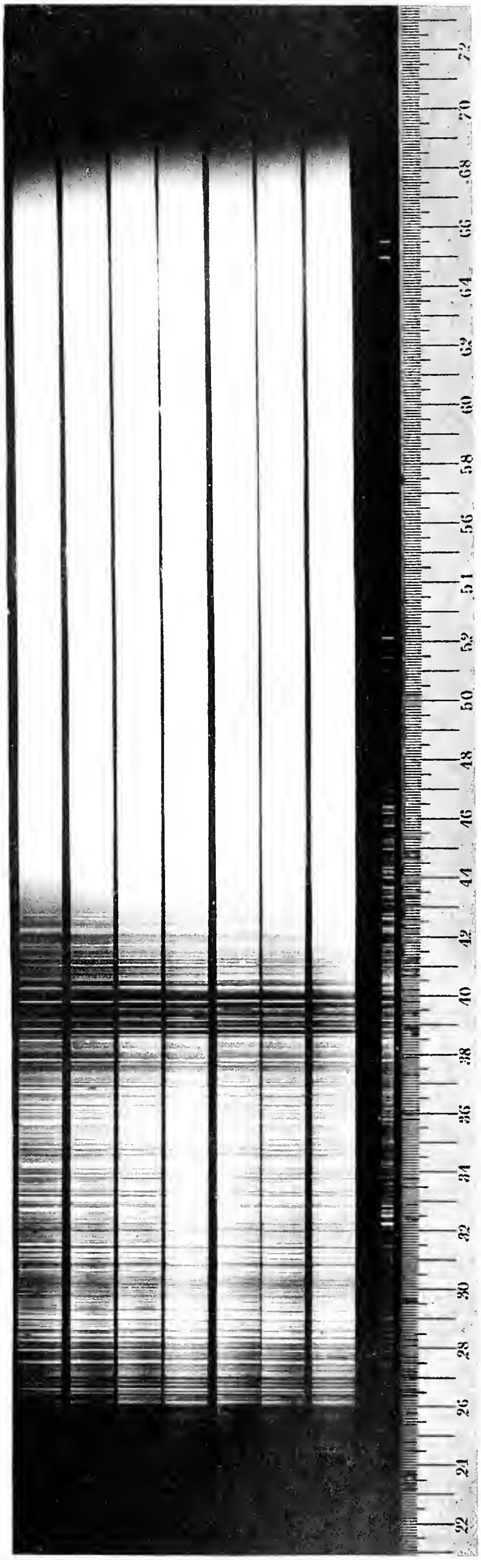

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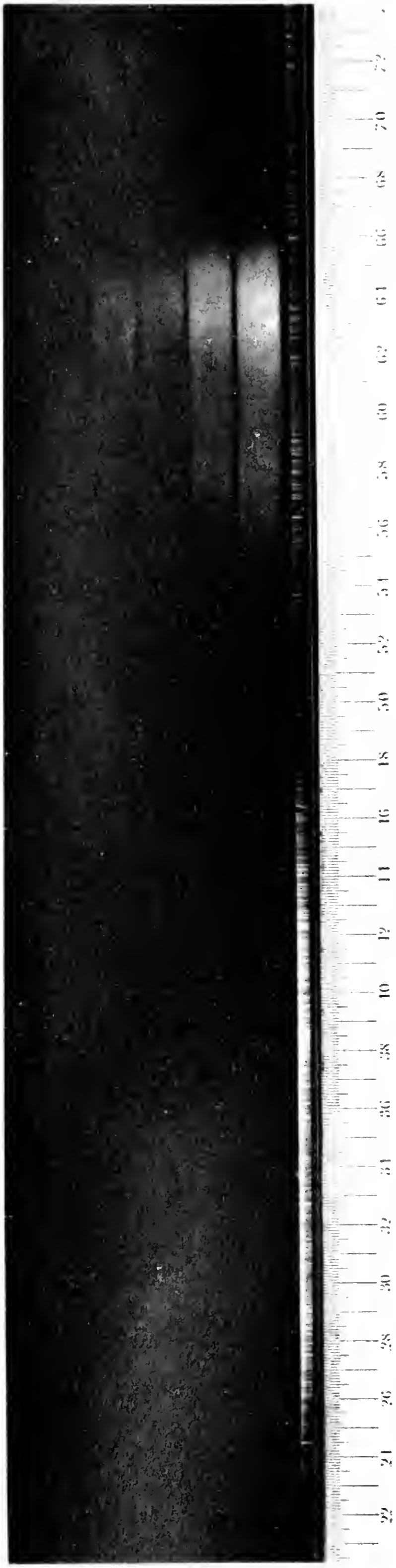
CAMPBELL ART CO., ELIZABETH, N. J



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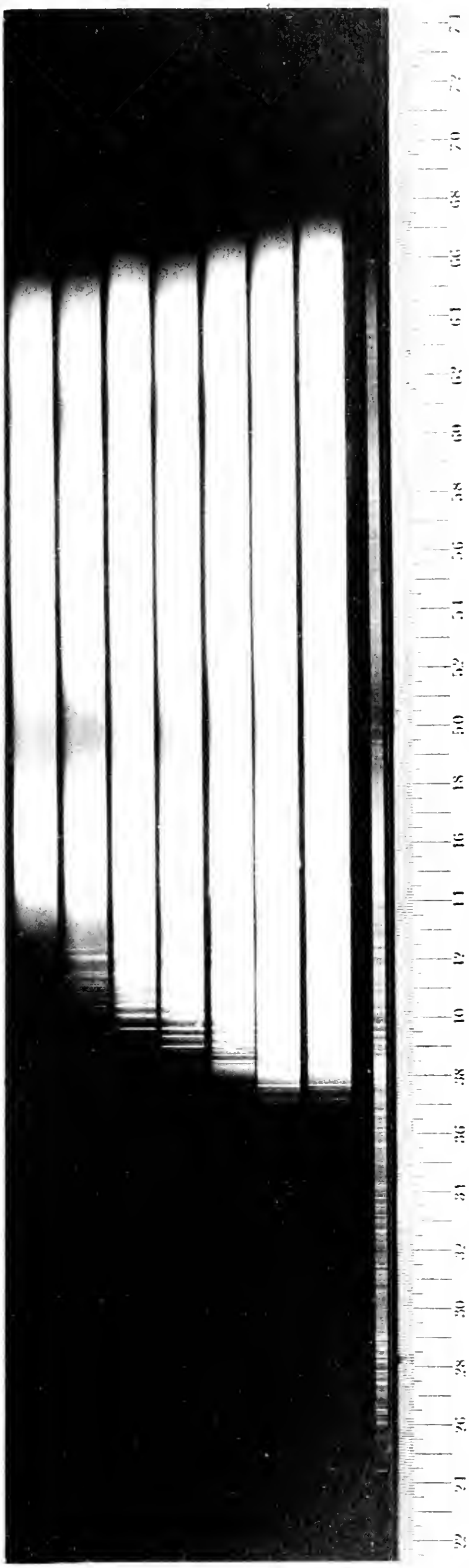

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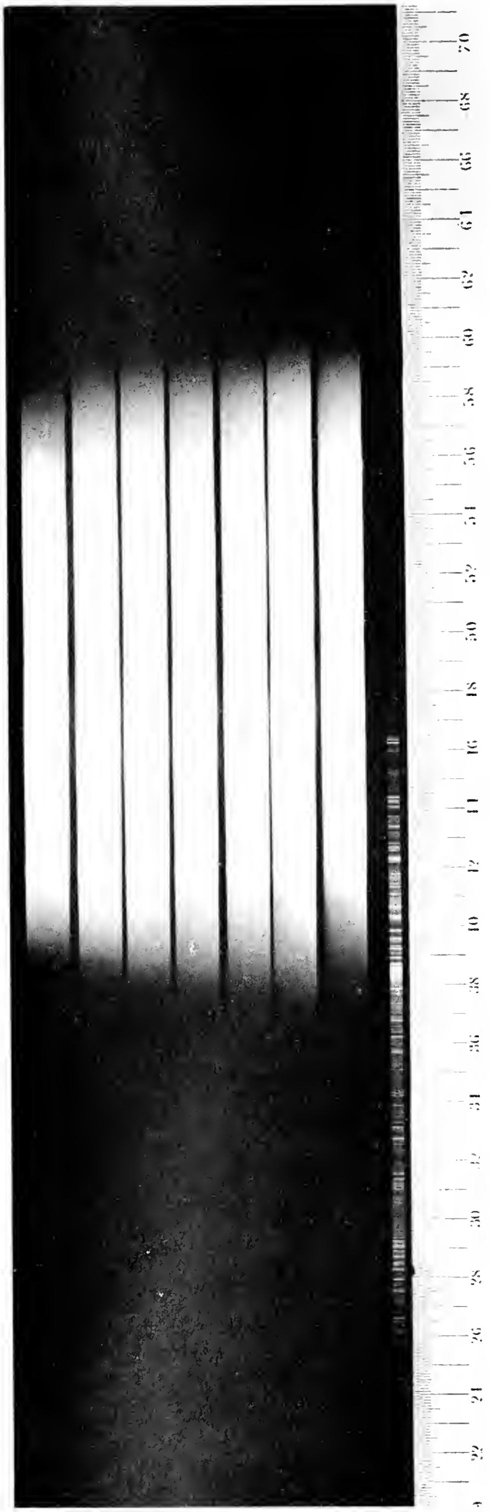
CAMPBELL ART CO., ELIZABETH, N.



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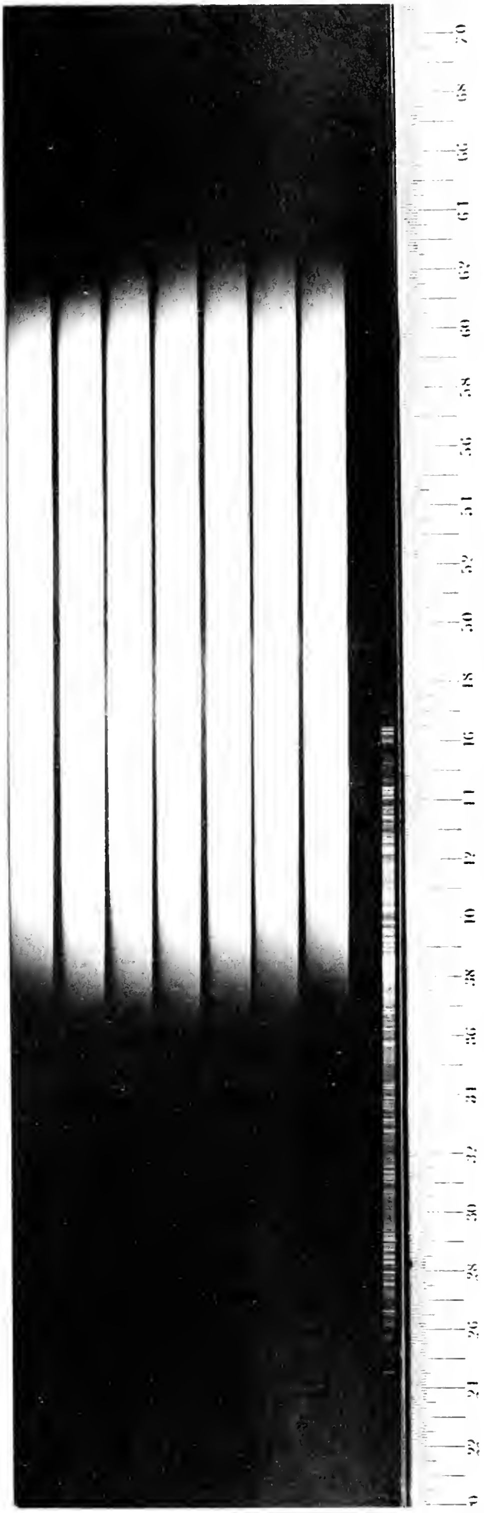

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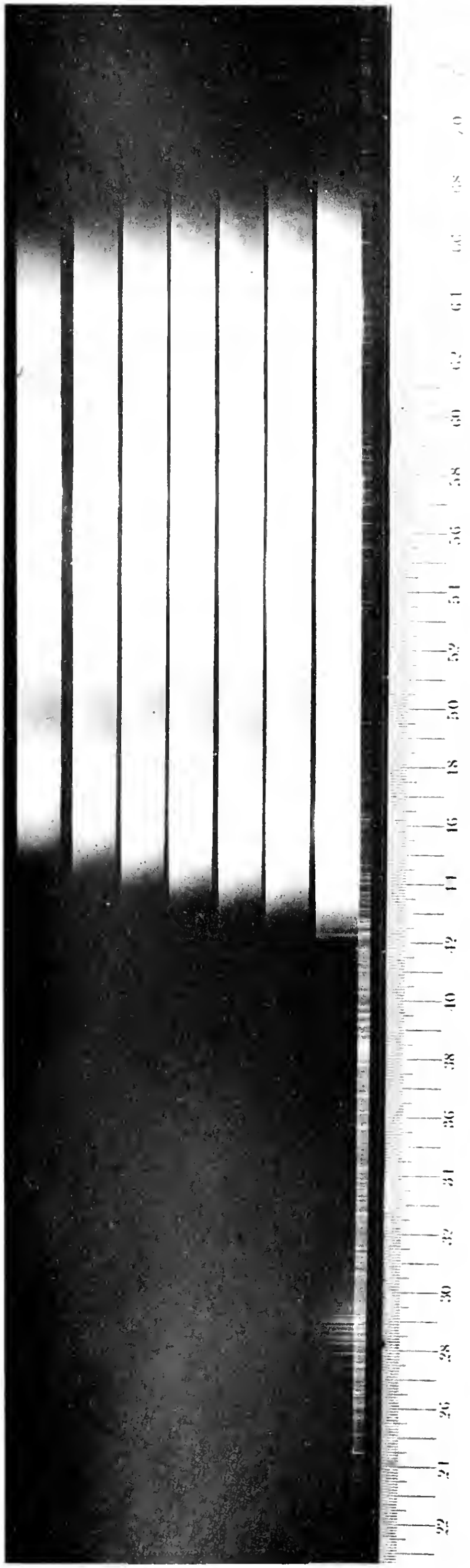
CAMPBELL ART CO., ELIZABETH, N. J

PLATE 25



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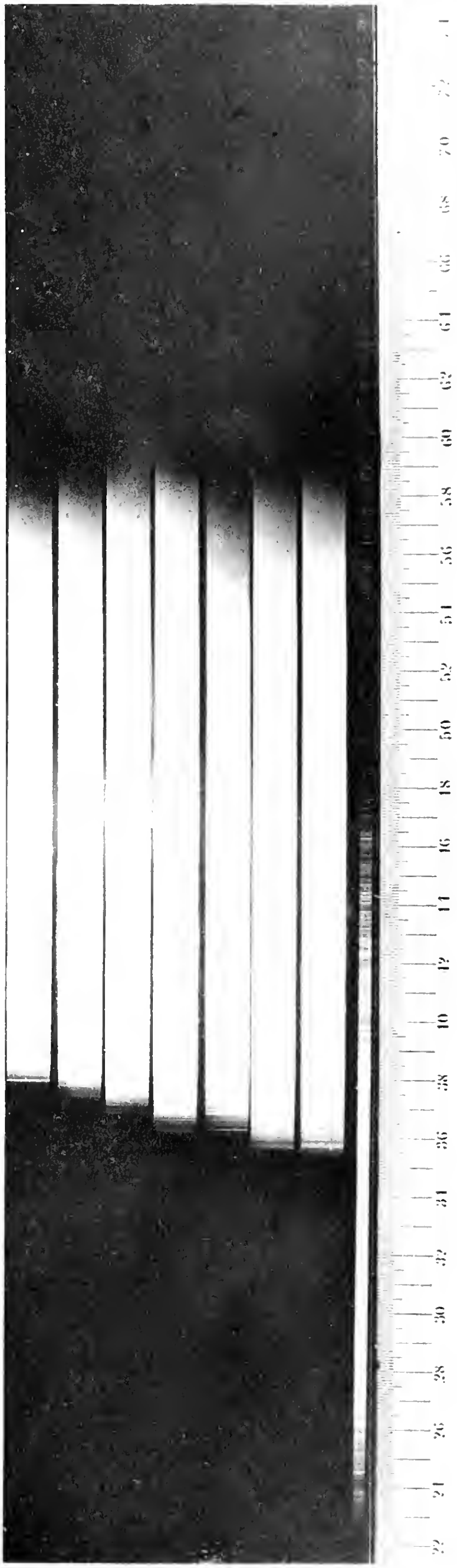

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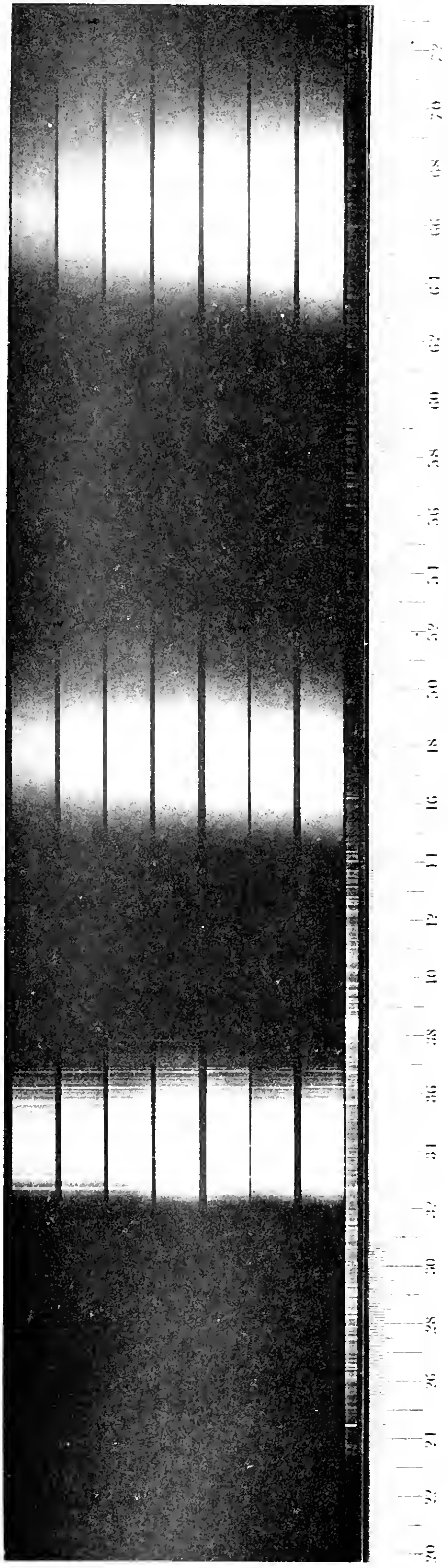
IPBELL ART CO., ELIZABETH, N. J.



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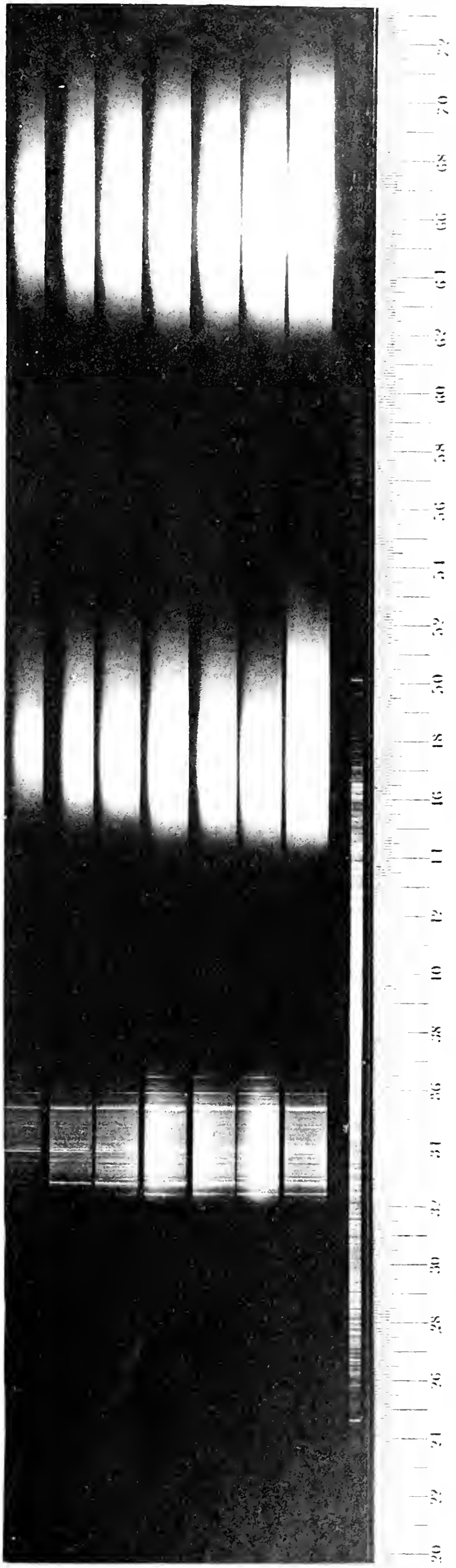

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CAMPBELL ART CO., ELIZABETH, N

PLATE 27

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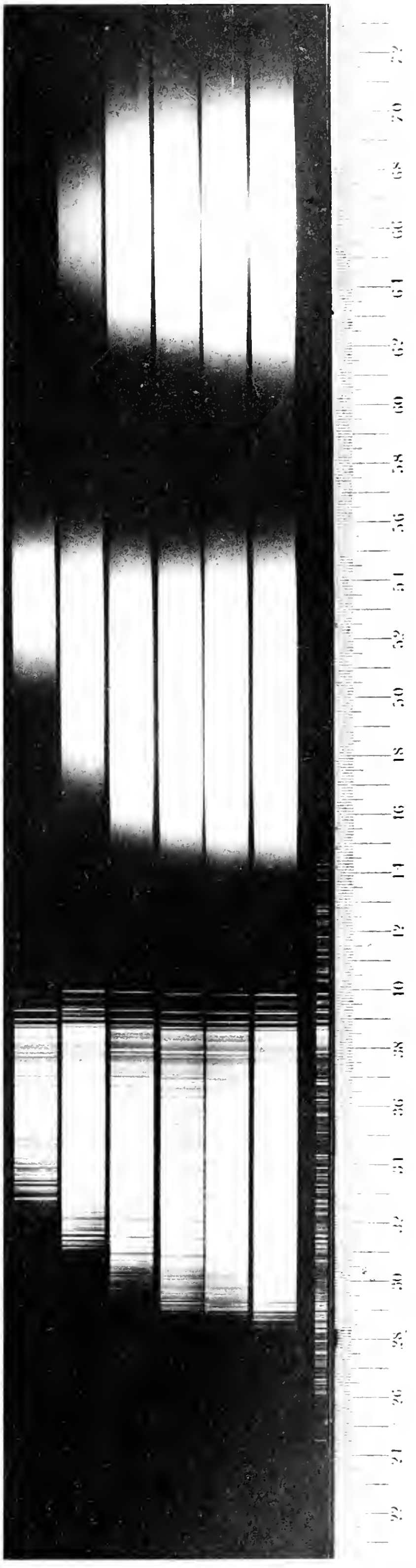

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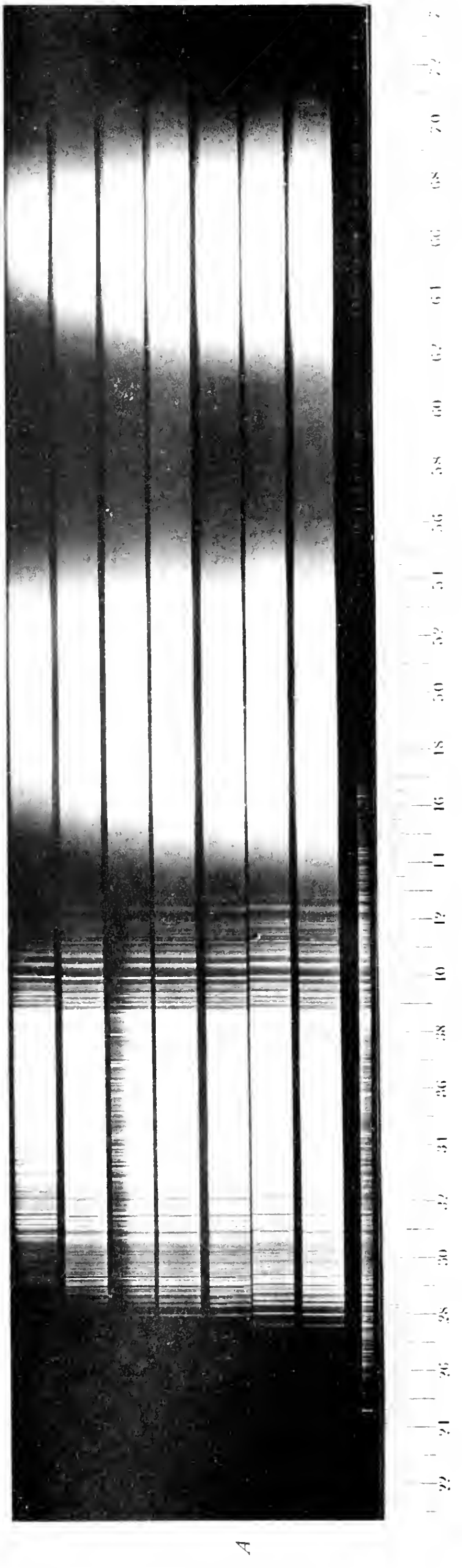
CAMPBELL ART CO., ELIZABETH, N. J.

PLATE 28



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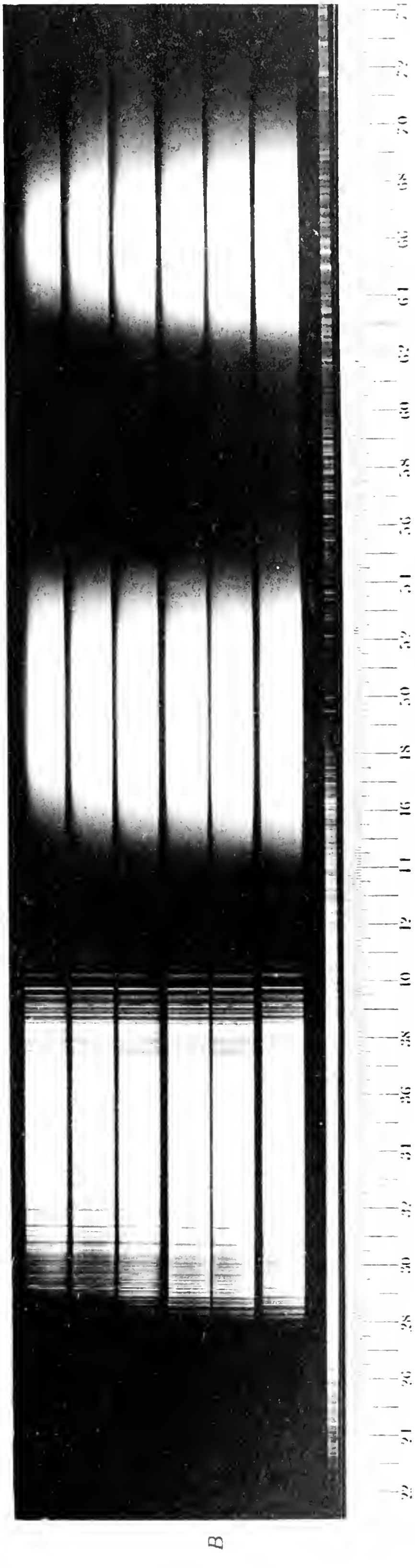

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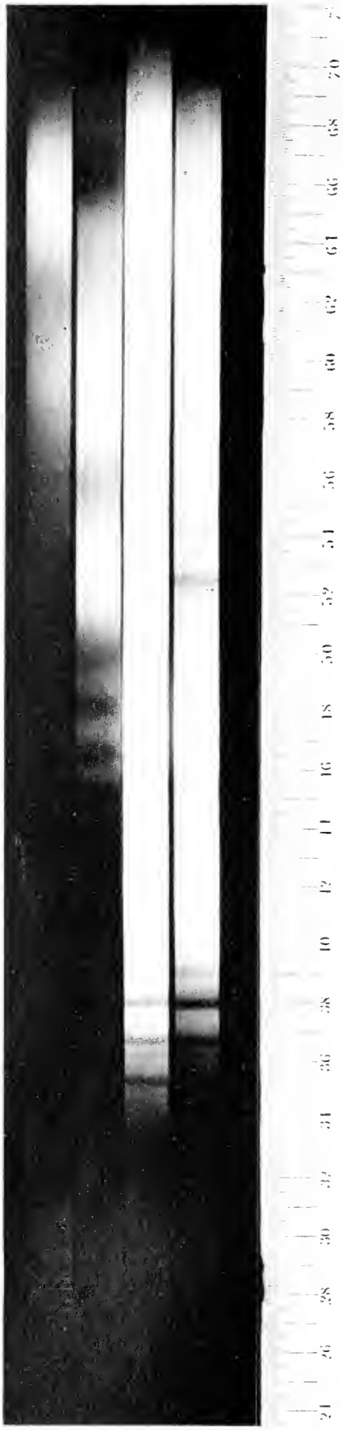
CAMPBELL ART CO., ELIZABETH, N. J.



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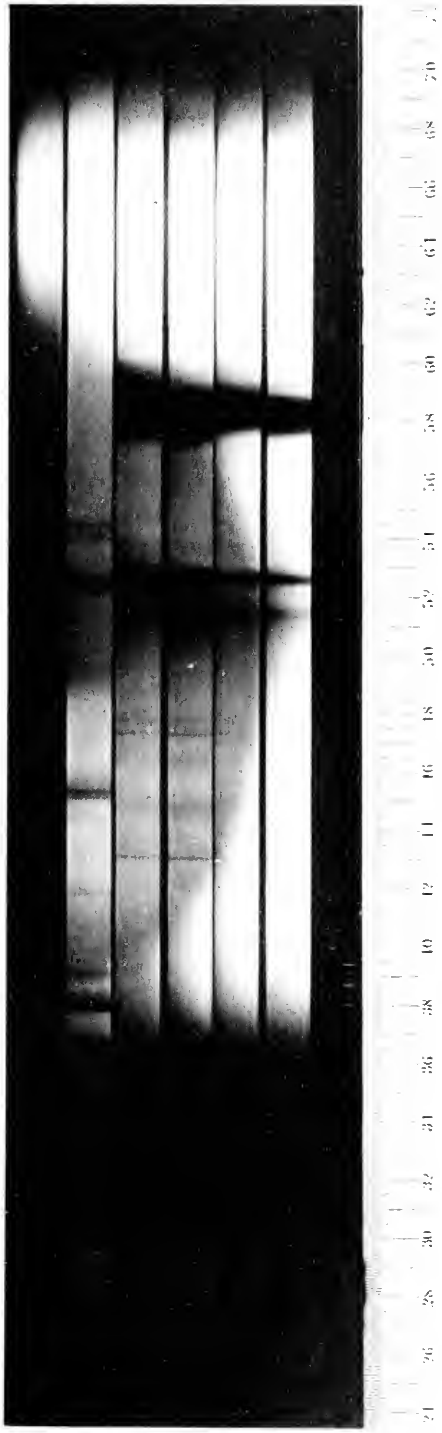

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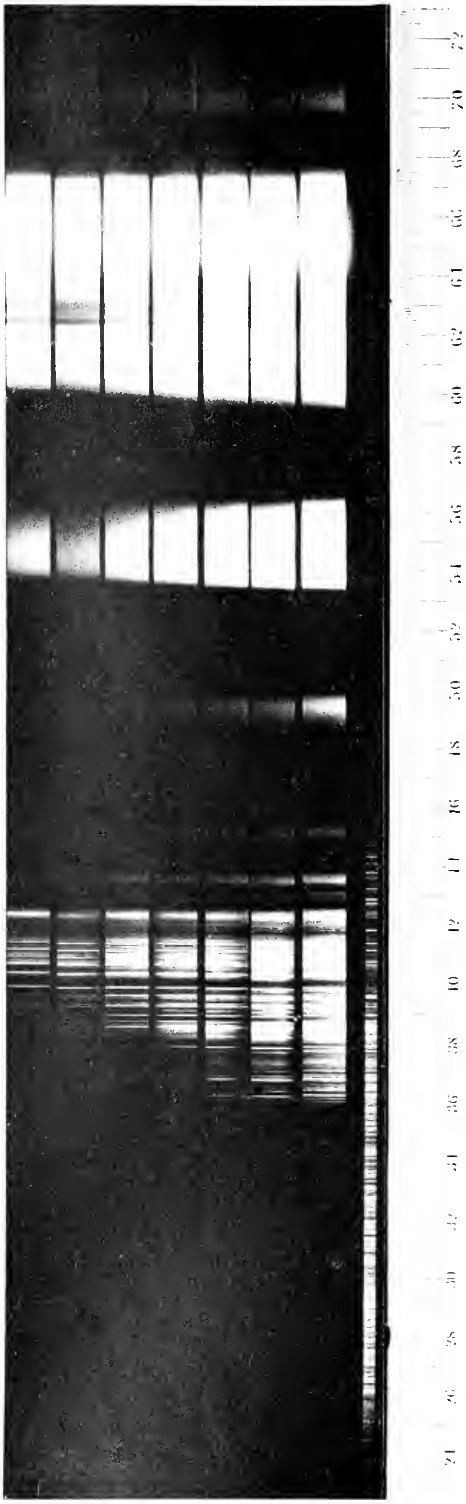
CAMPBELL ART CO., ELIZABETH, N. J.



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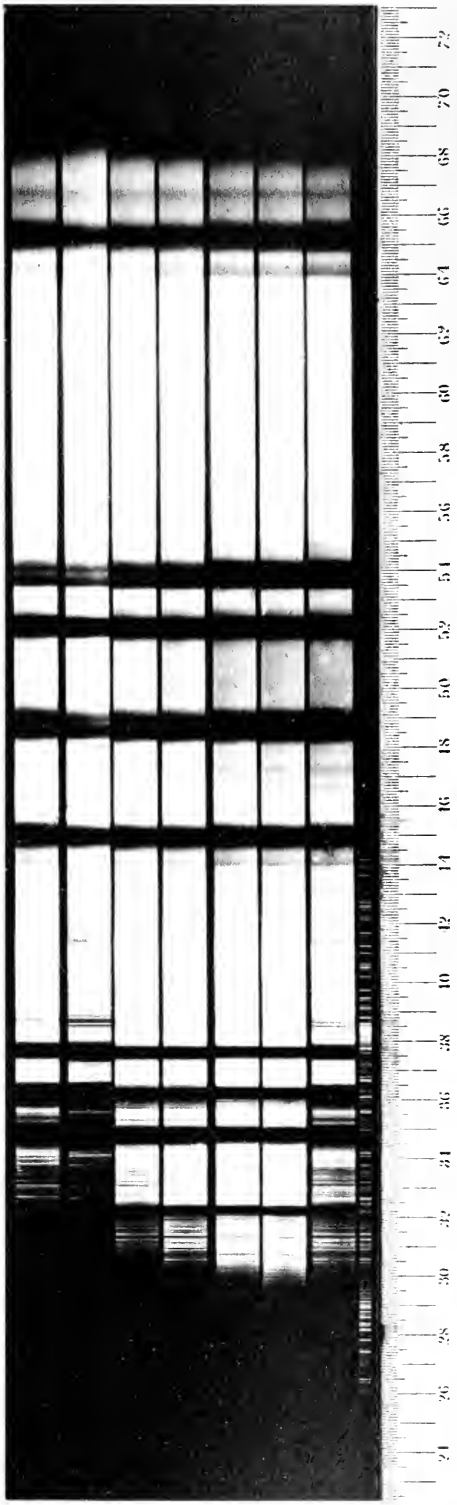

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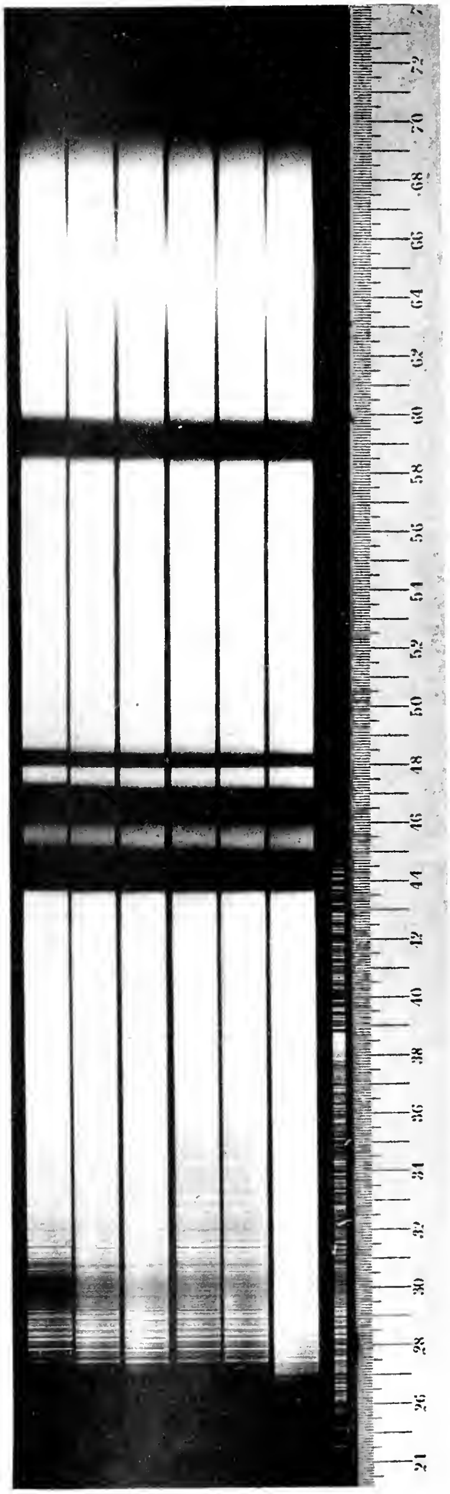
CAMPBELL ART CO., ELIZABETH, N. J.



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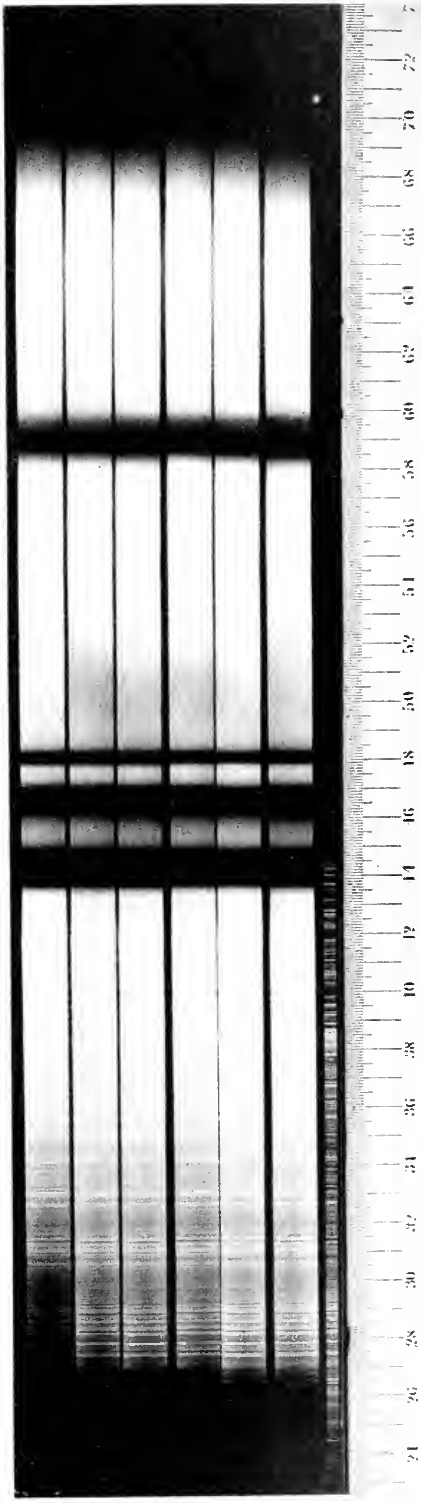

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CAMPBELL ART CO., ELIZABETH, N. J.

CAMPBELL ART CO., ELIZABETH, N. J.

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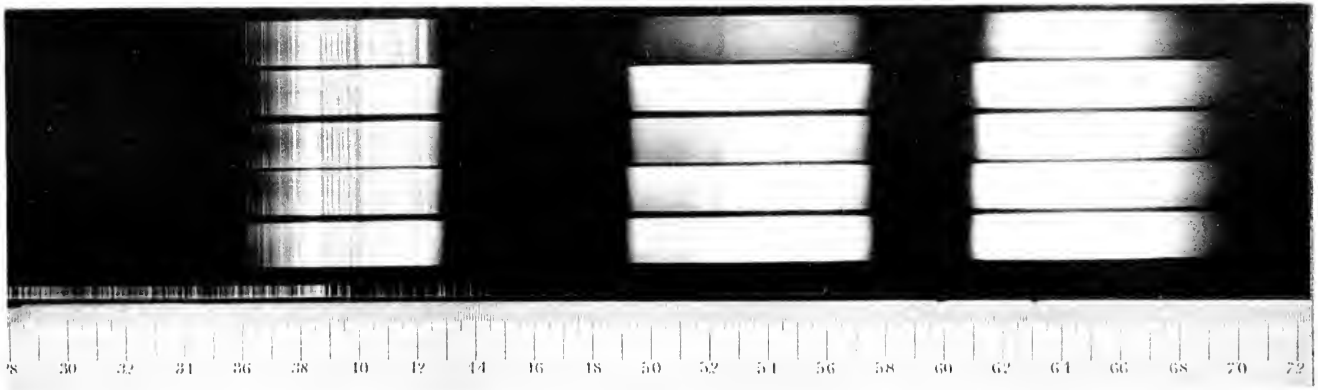

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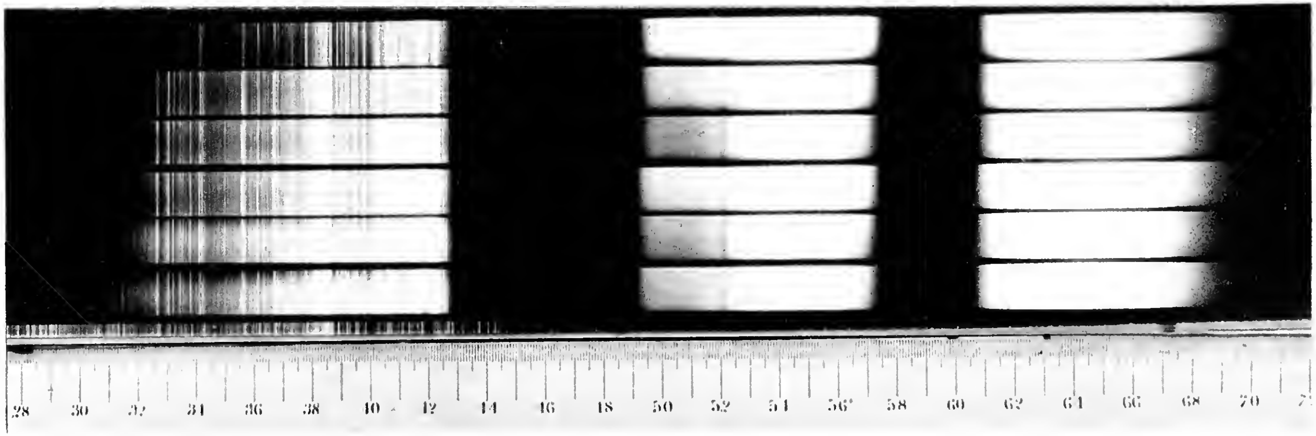
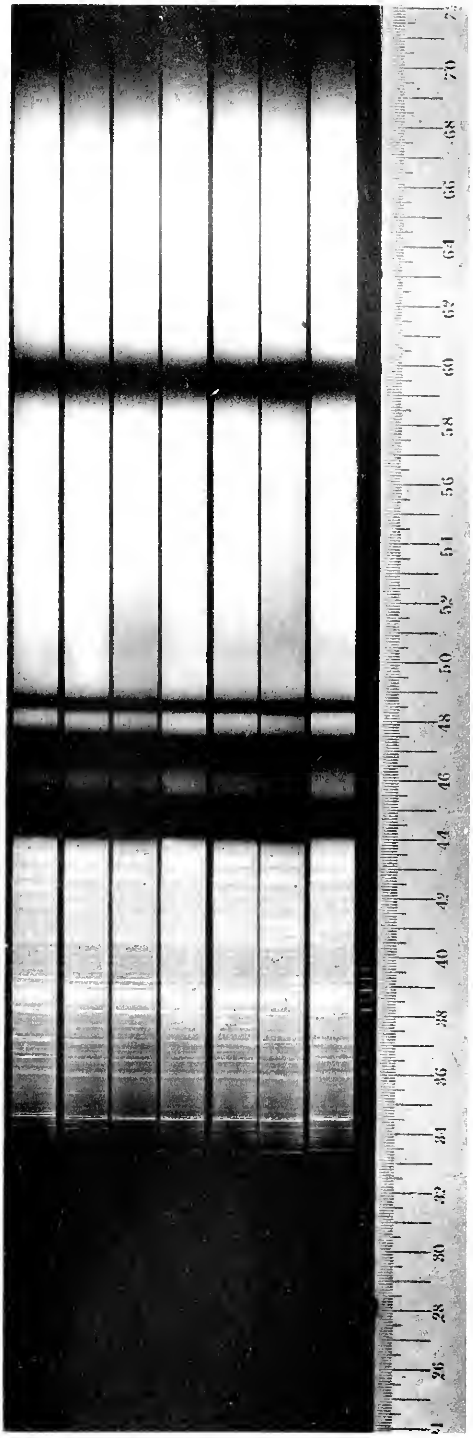


PLATE 32



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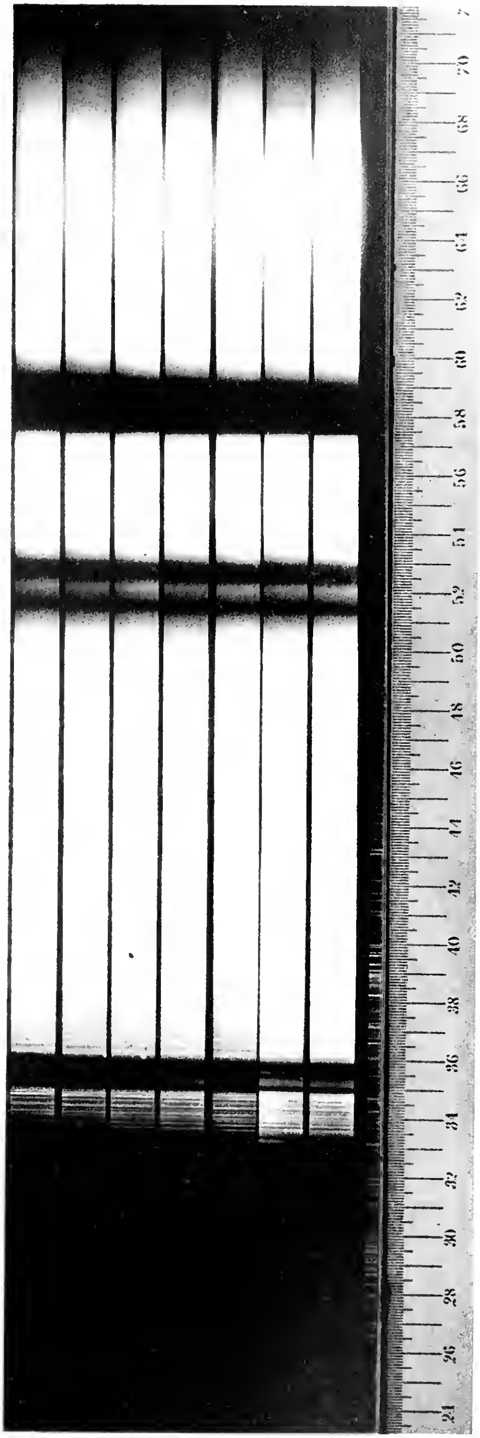

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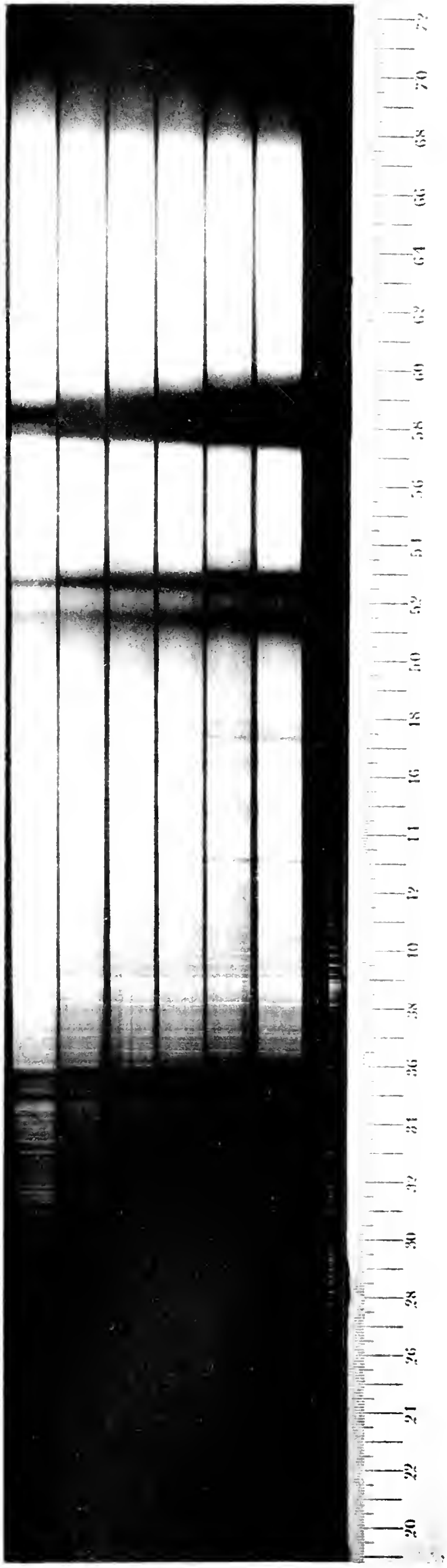
CAMPBELL ART CO., ELIZABETH, N. J.



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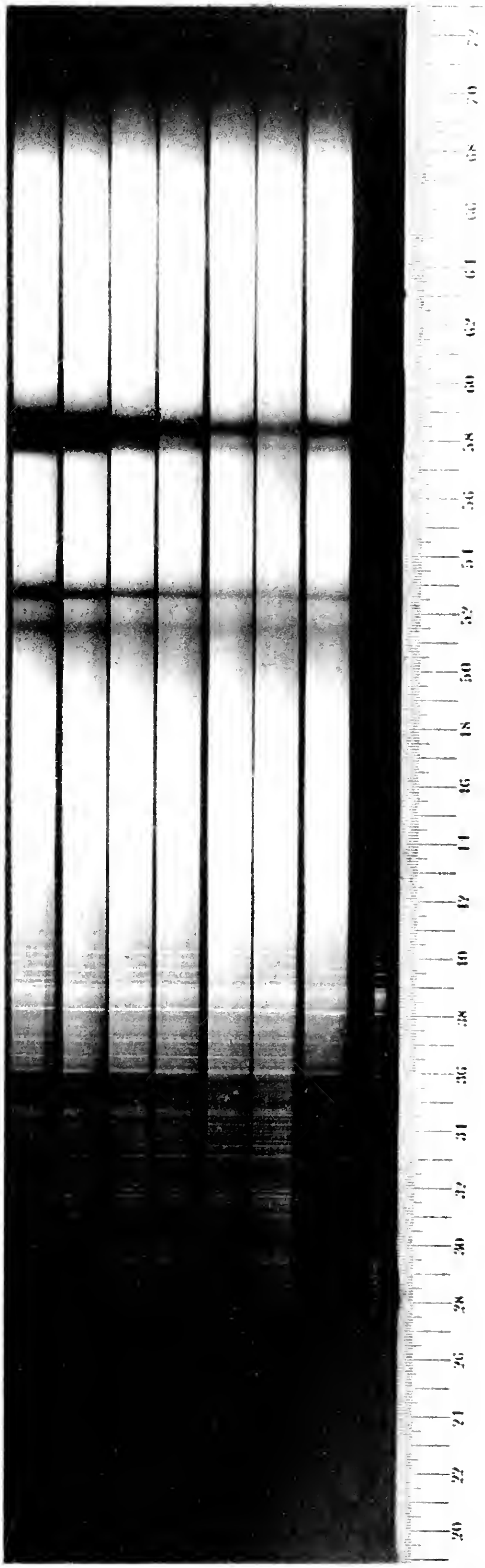

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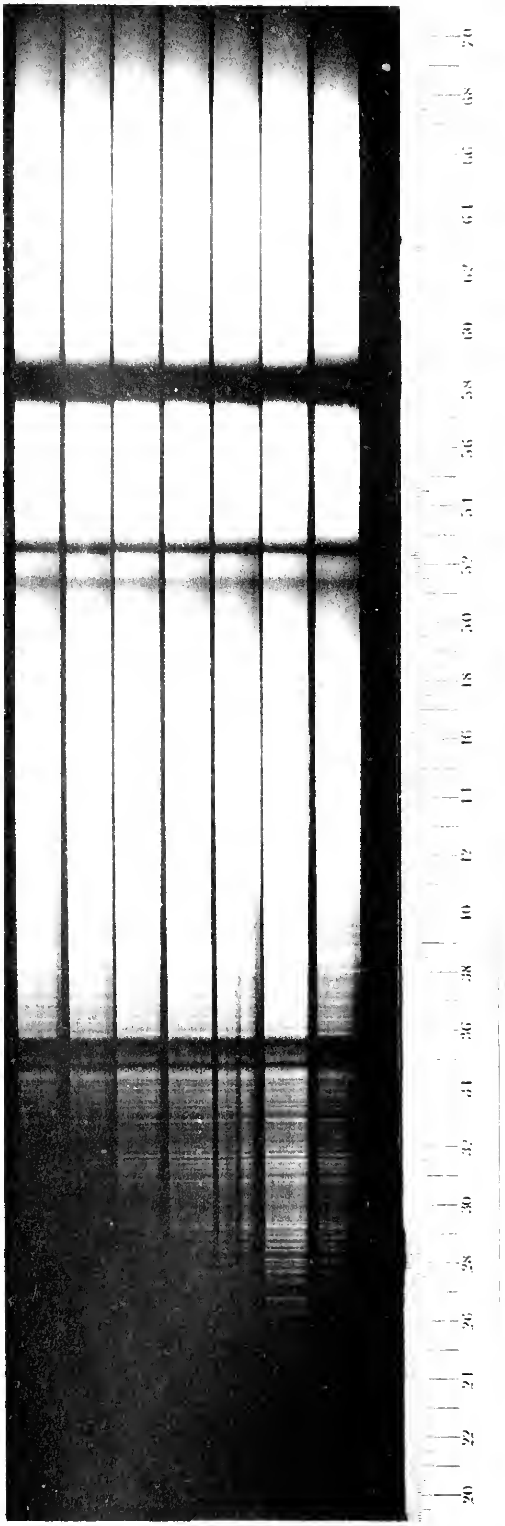

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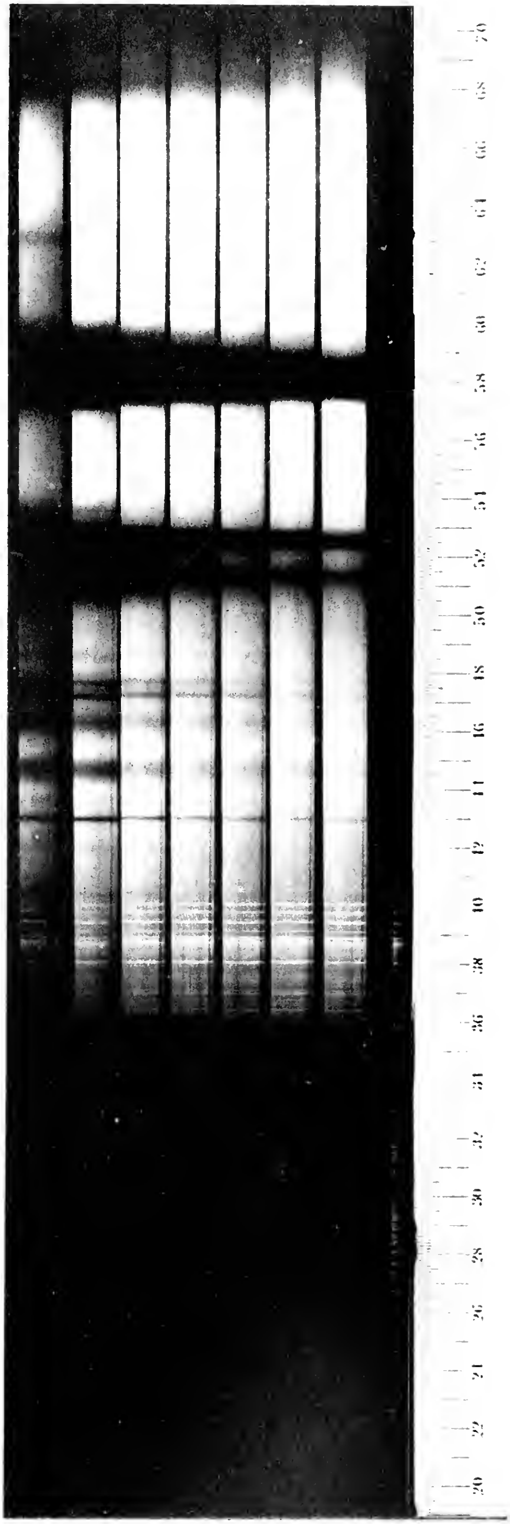

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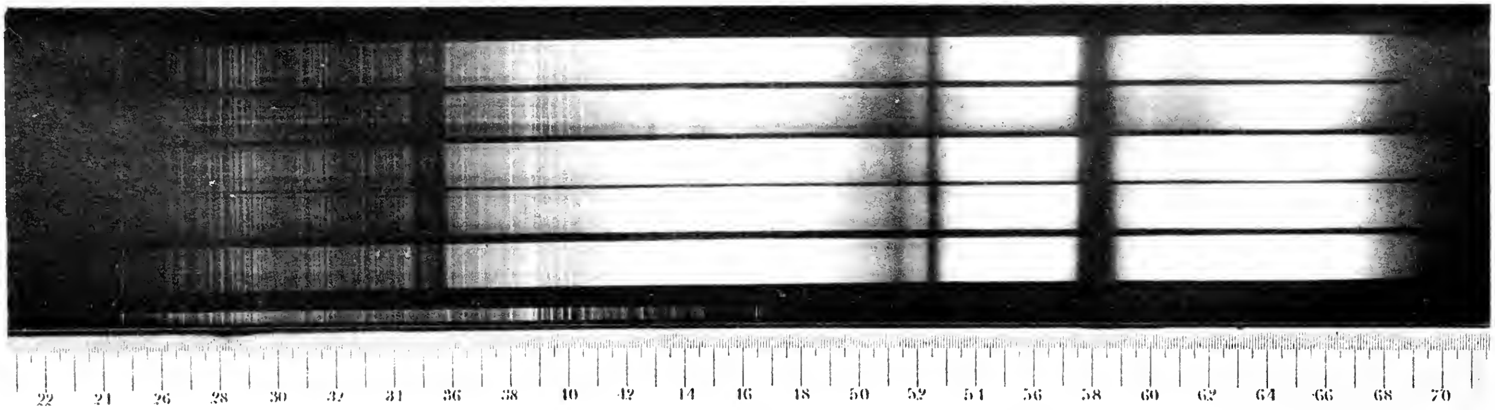
CAMPBELL ART CO., ELIZABETH, N. J.



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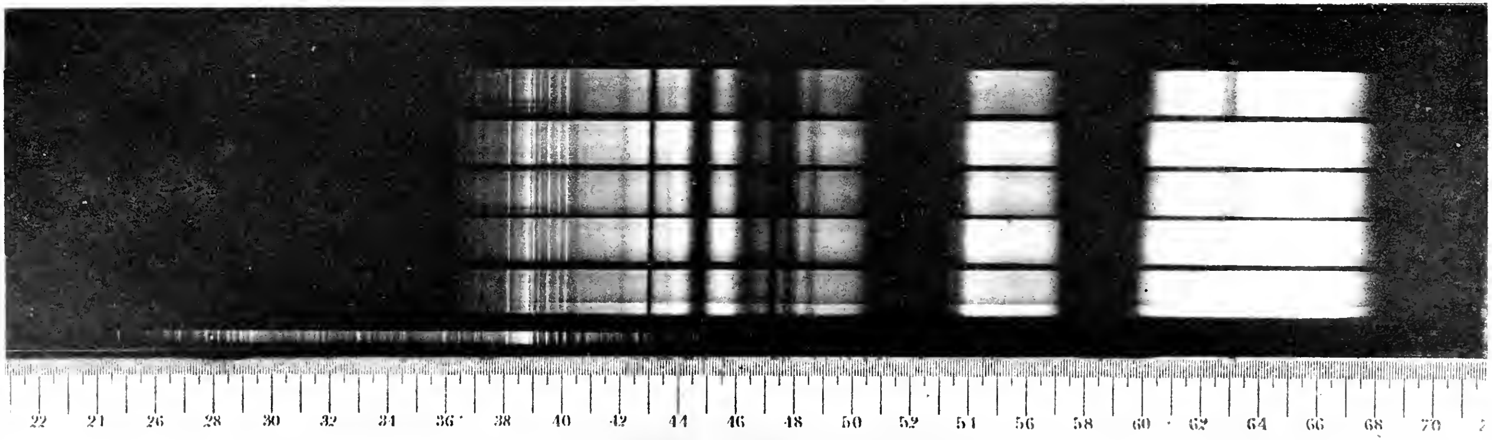

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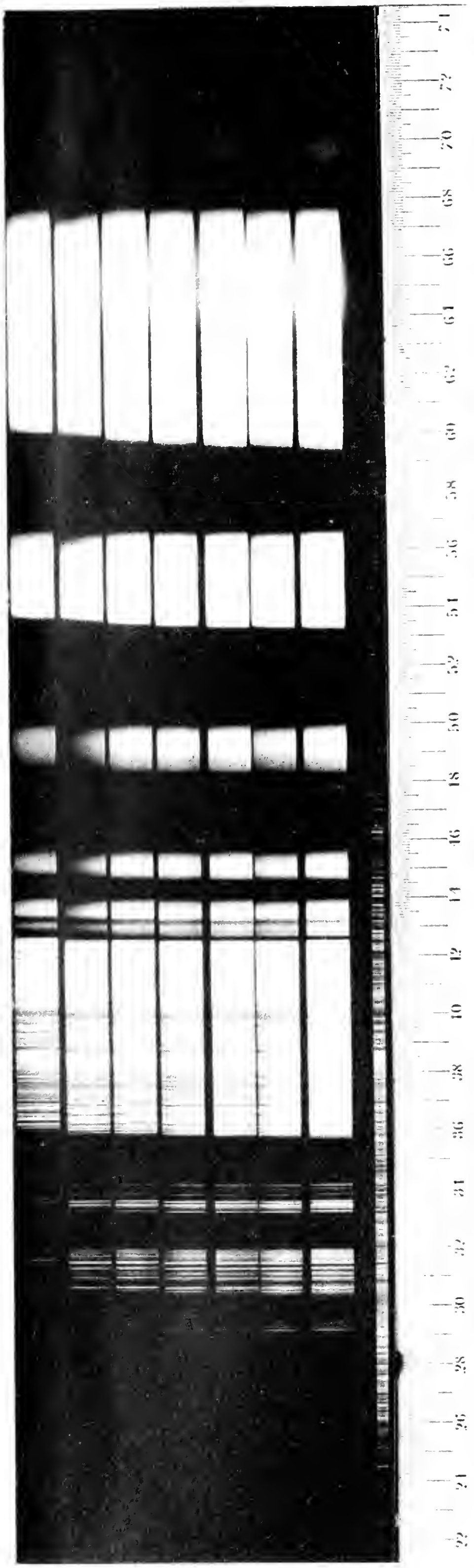

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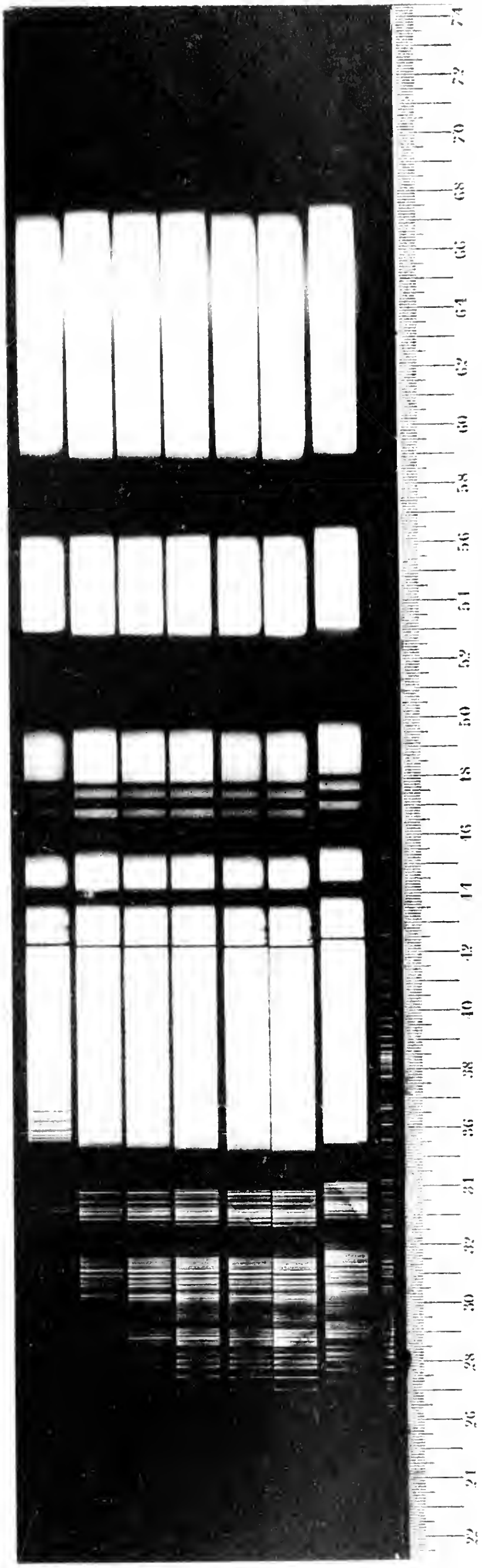

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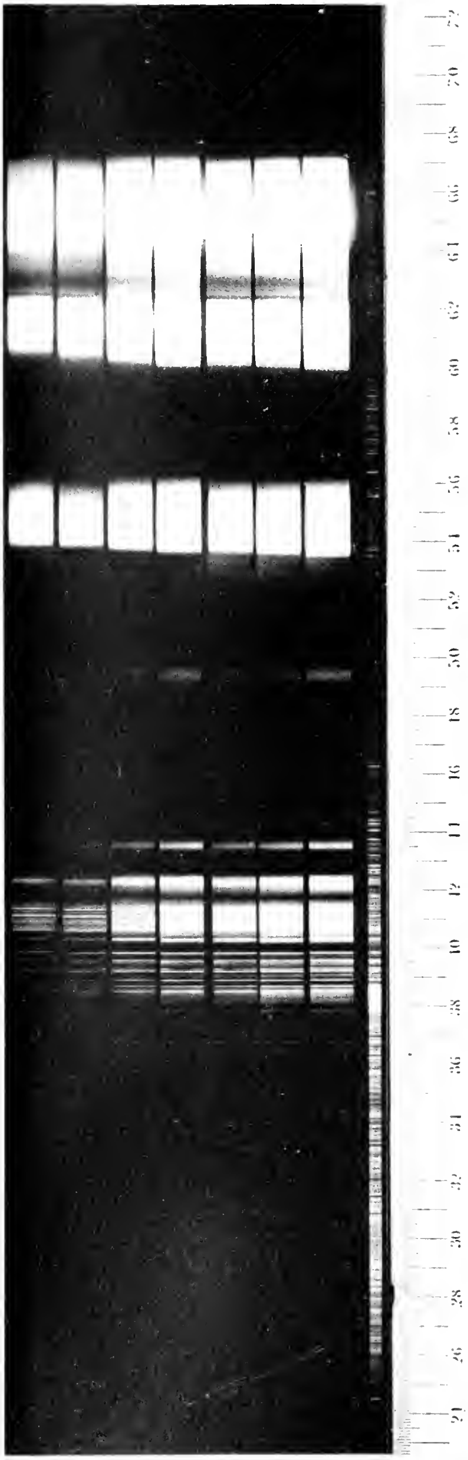
CAMPBELL ART CO., ELIZABETH, N. J.



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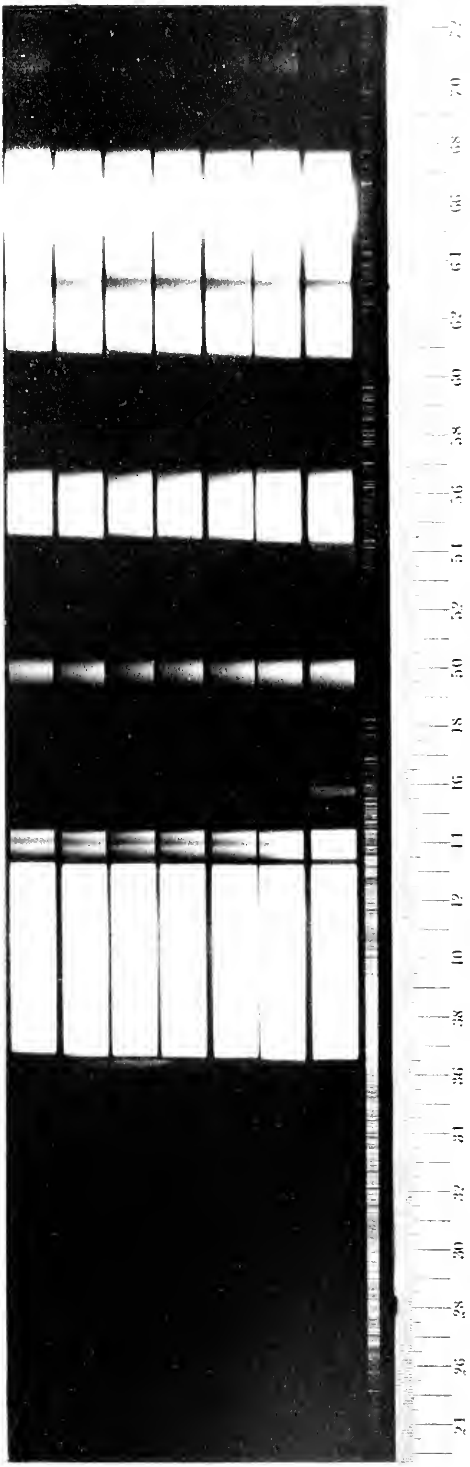

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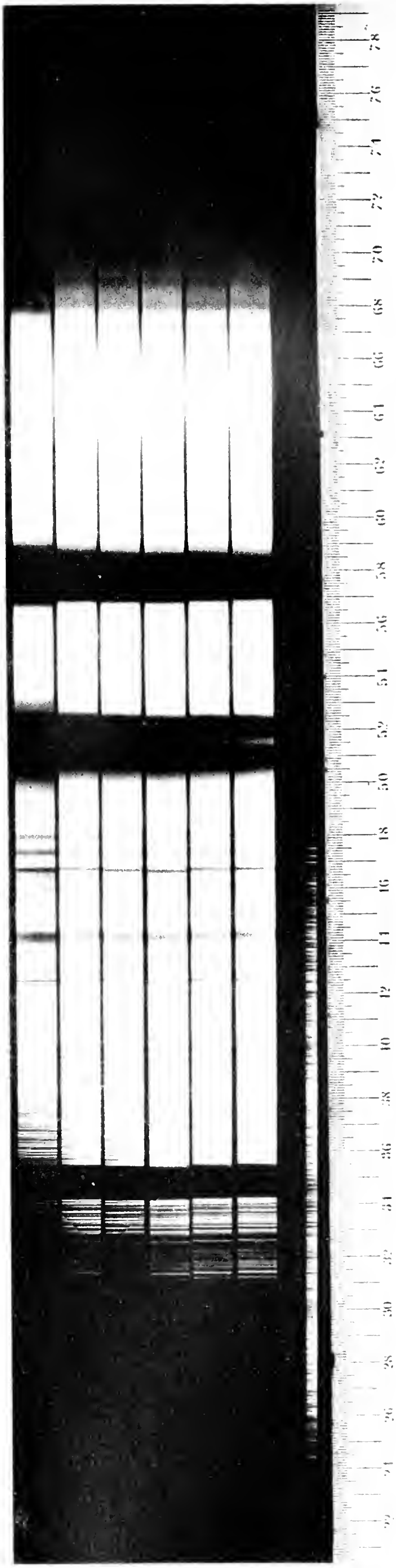
CAMPBELL ART CO., ELIZABETH, N. J.



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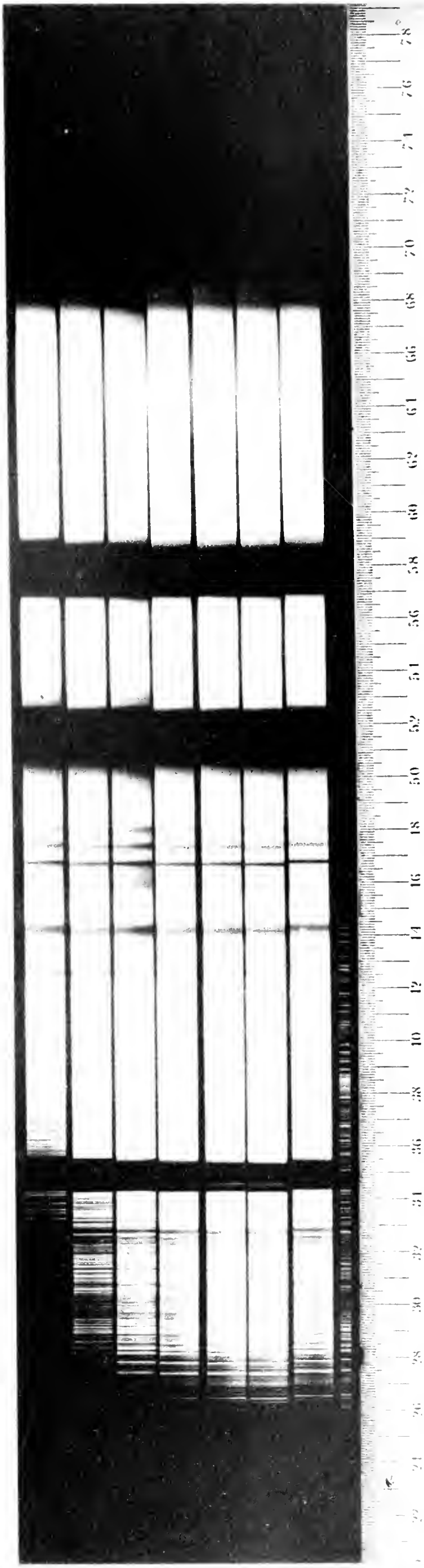

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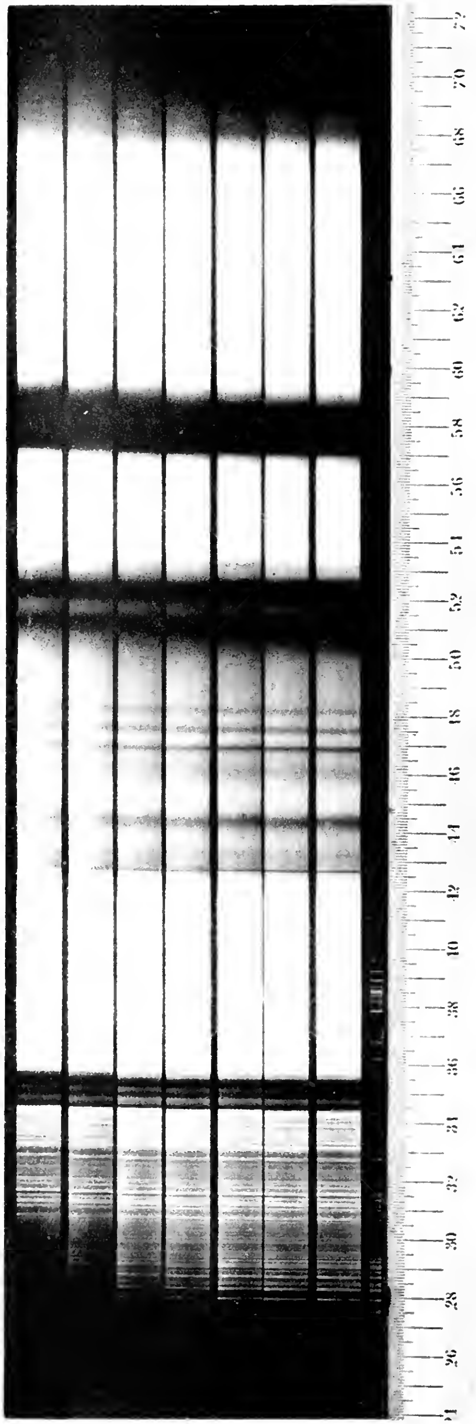
CAMPBELL ART CO., ELIZABETH, N. J.



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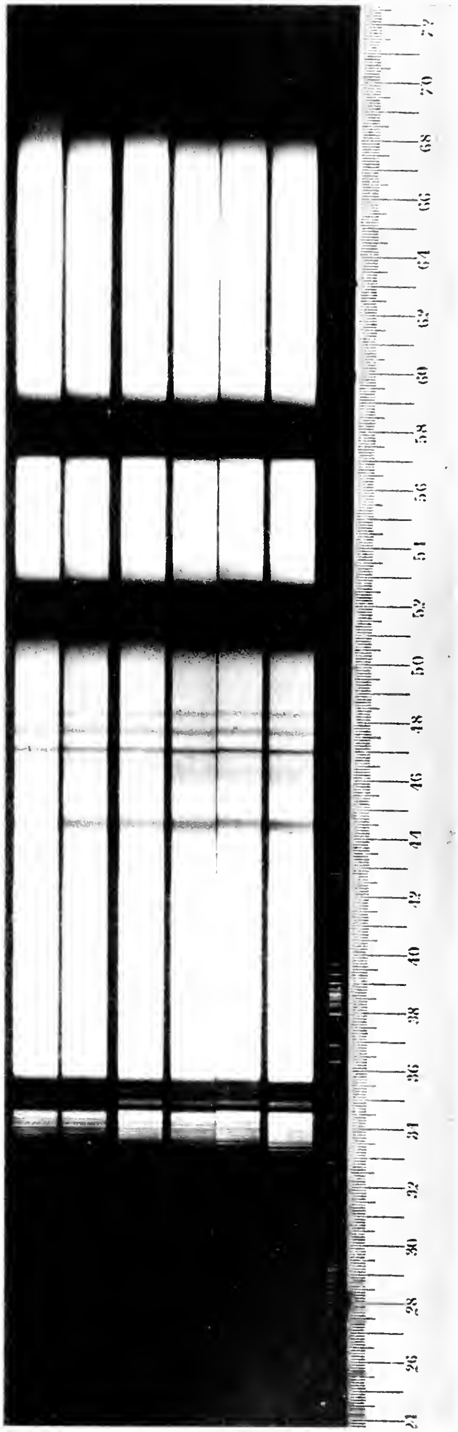

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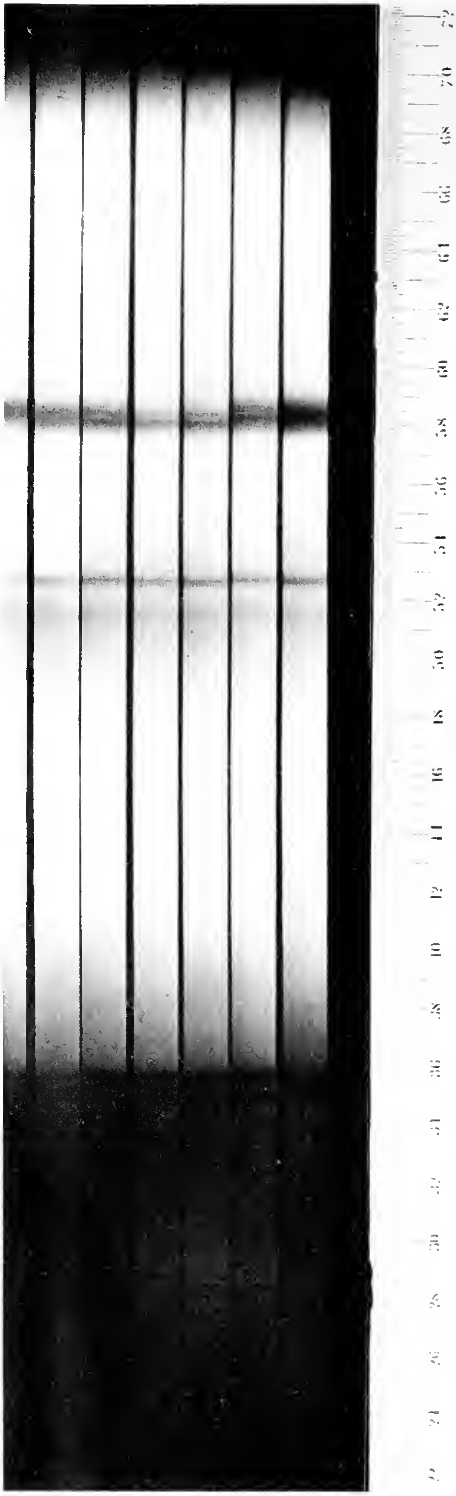
CAMPBELL ART CO., ELIZABETH, N. J.



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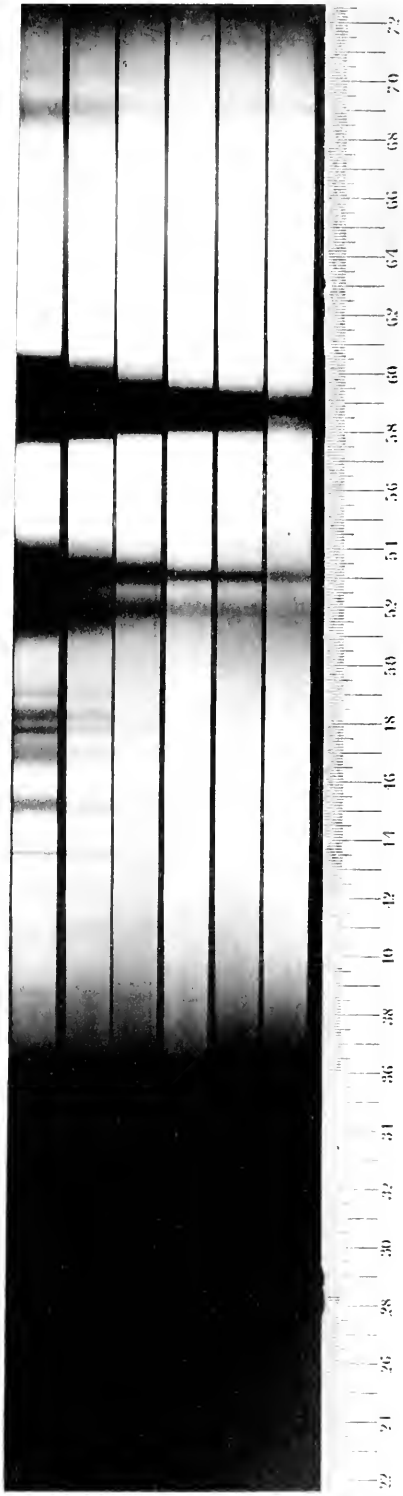

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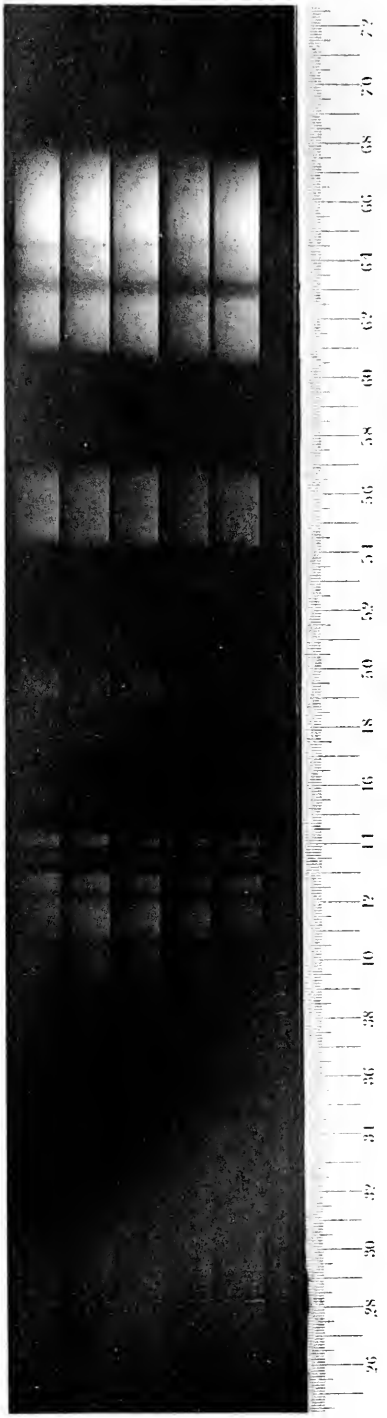
CAMPBELL ART CO., ELIZABETH, N. J.

PLATE 42



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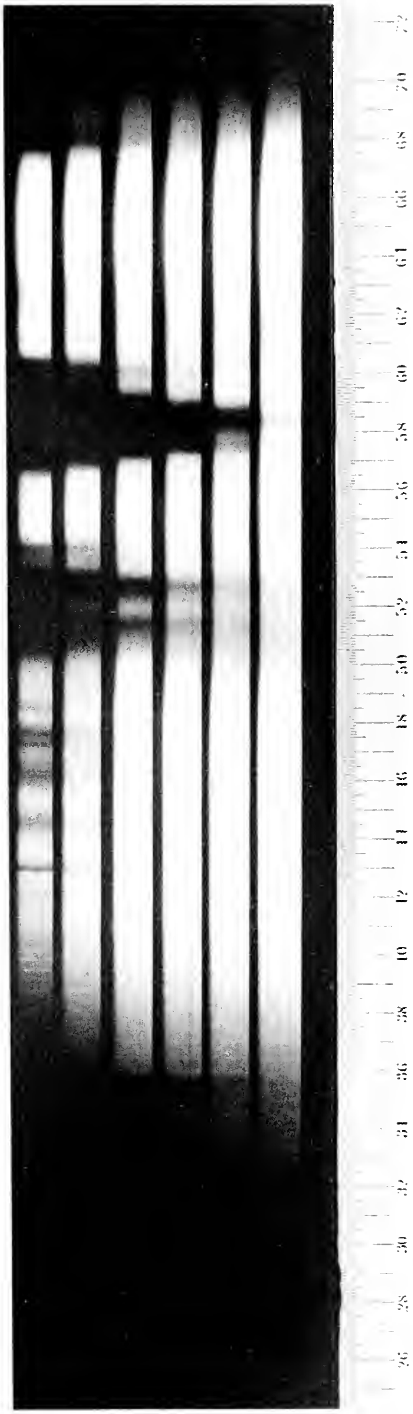

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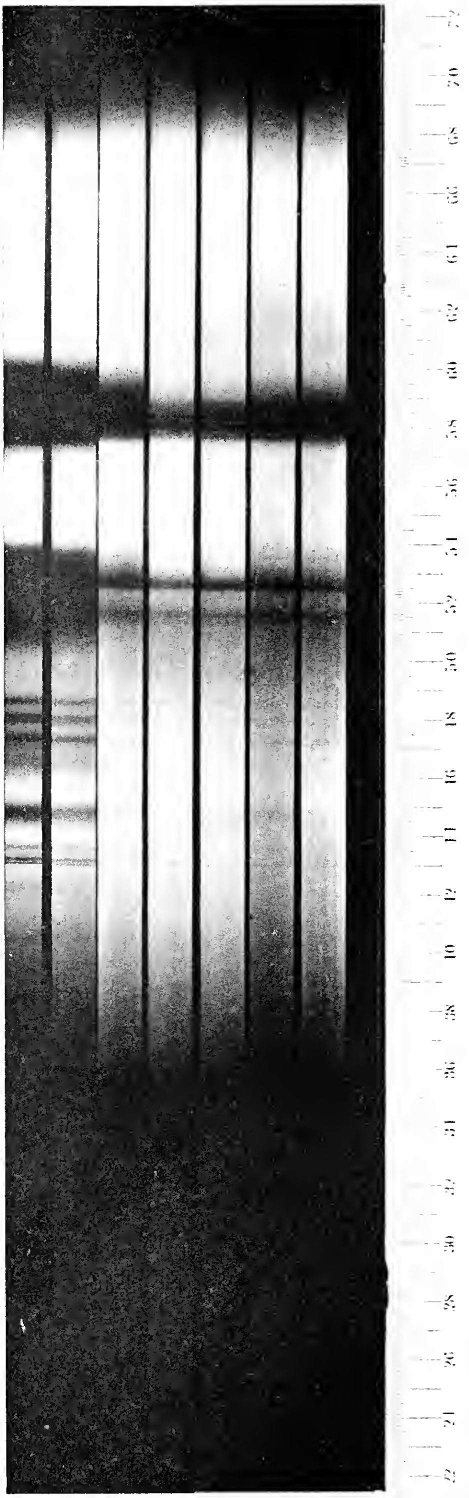
CAMPBELL ART CO., ELIZABETH, N. J.



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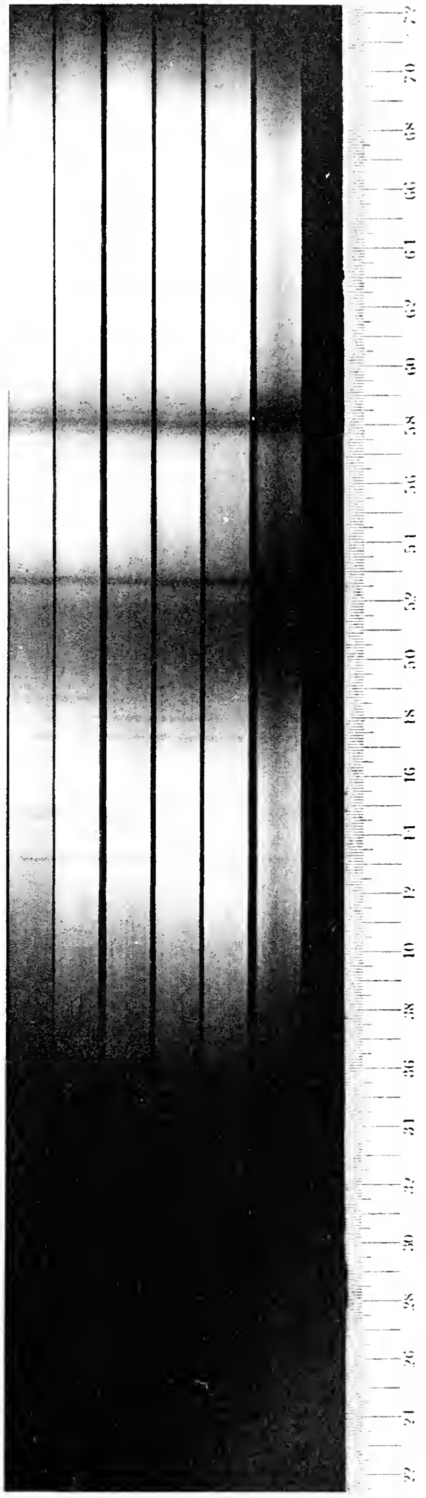

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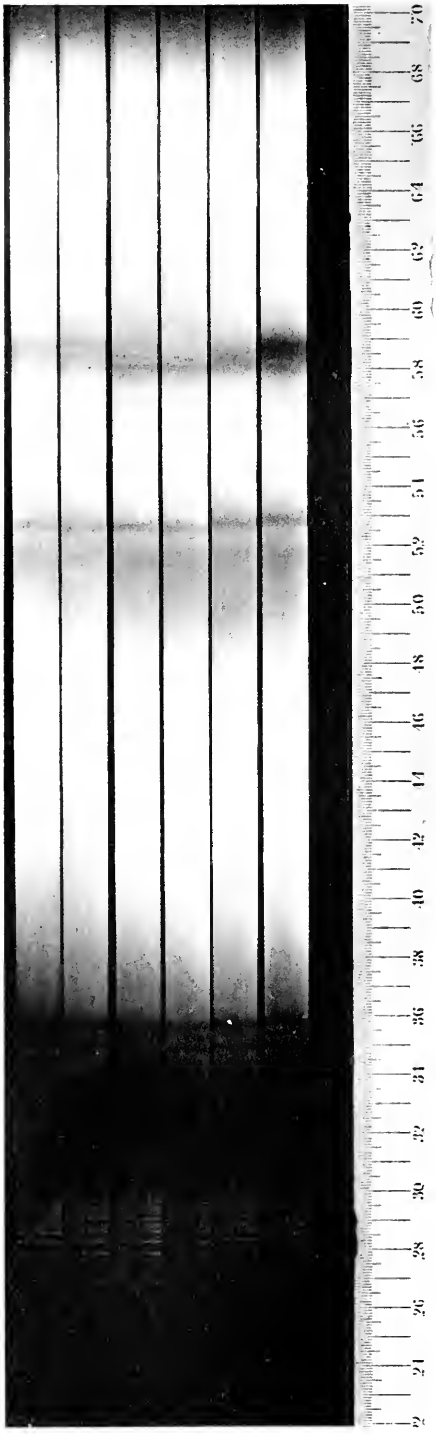
CAMPBELL ART CO., ELIZABETH, N. J.



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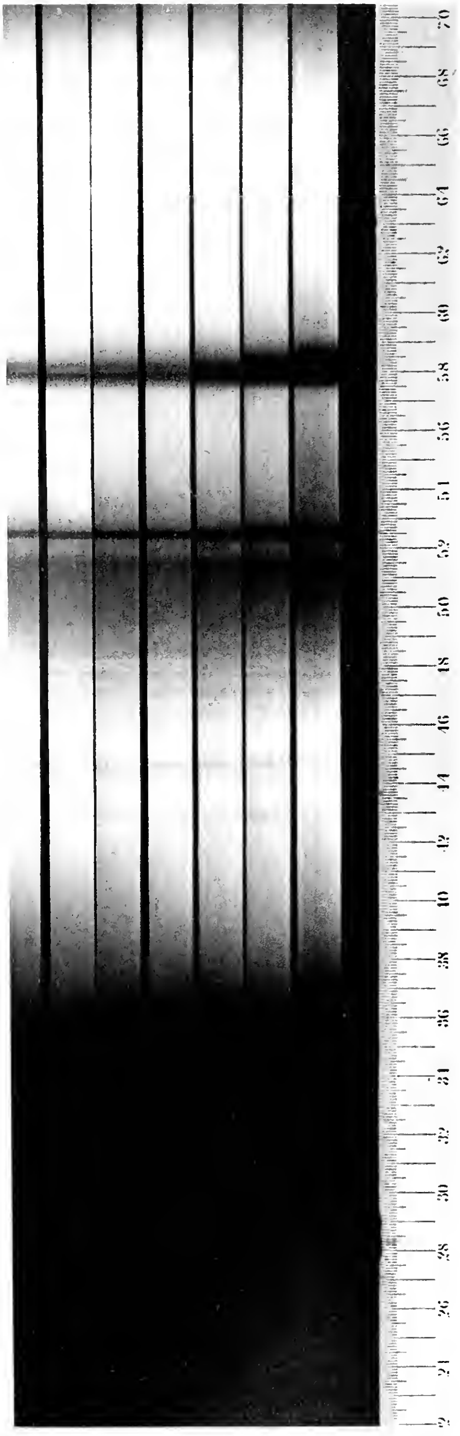

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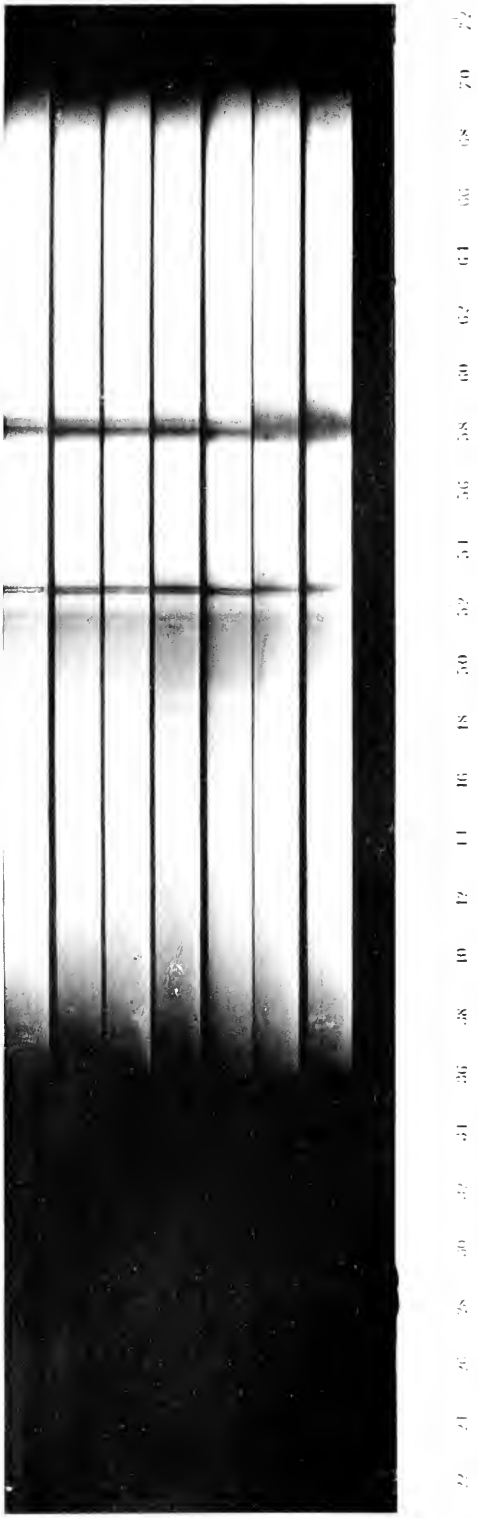
CAMPBELL ART CO., ELIZABETH, N. J.



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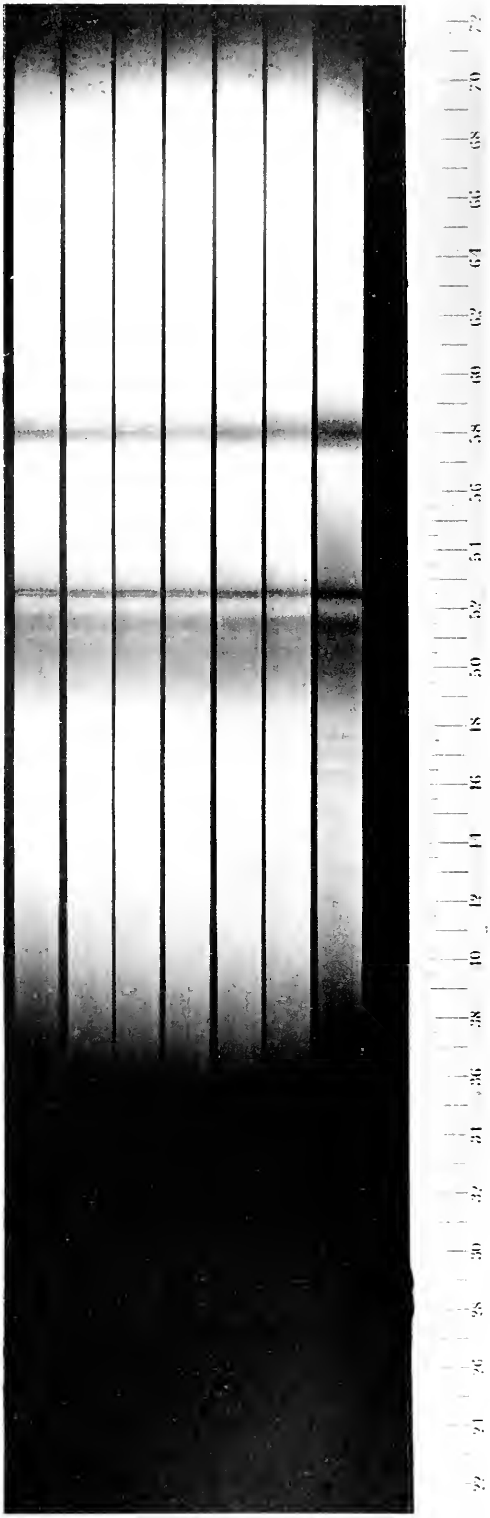

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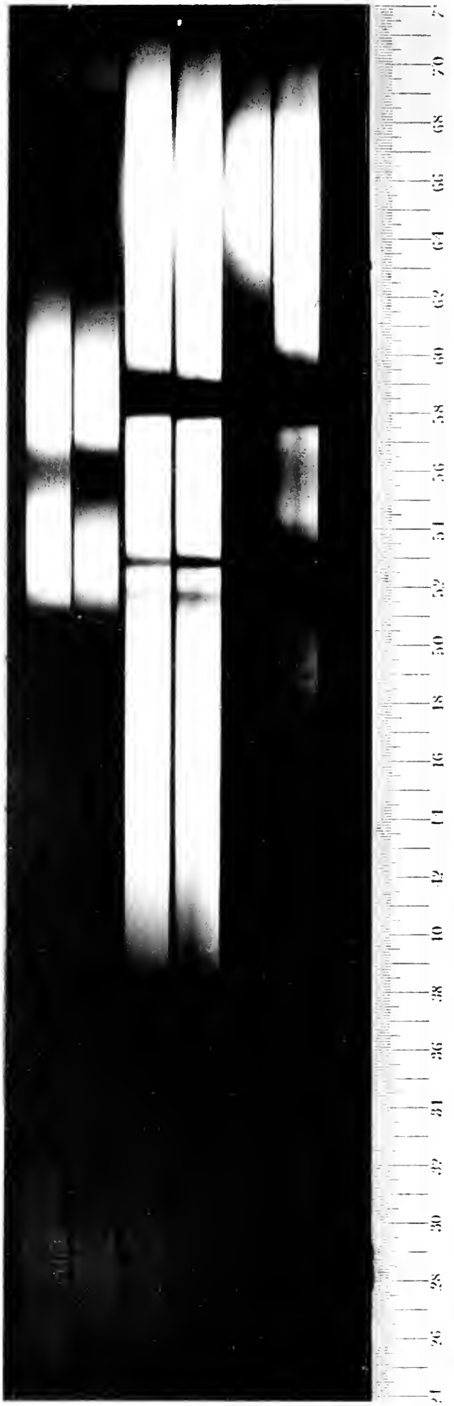
CAMPBELL ART CO., ELIZABETH, N

PLATE 46



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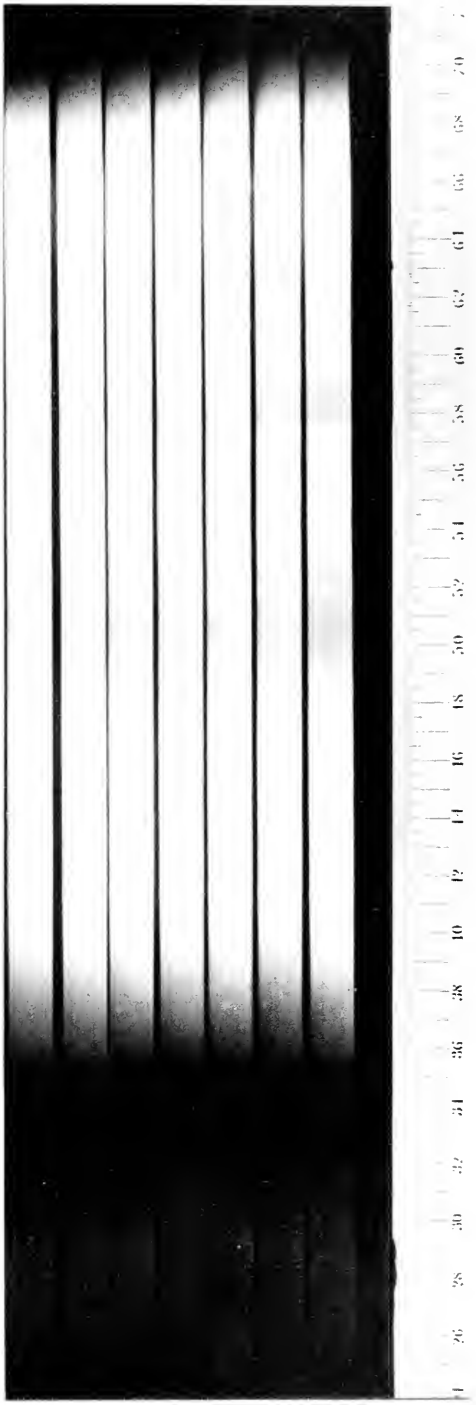
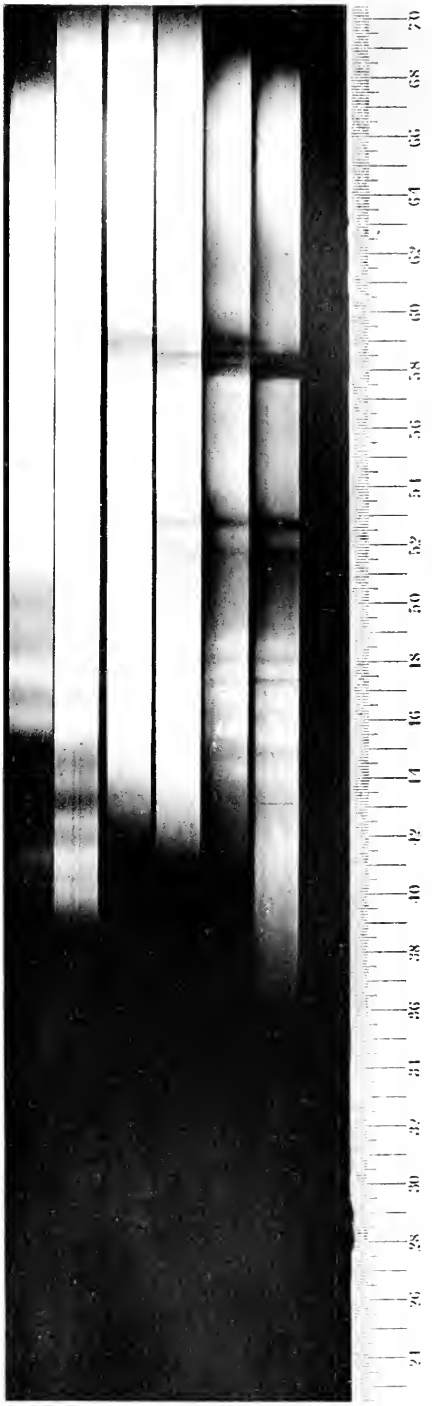


B

CAMPBELL ART CO., ELIZABETH, N. J.

PLATE 47



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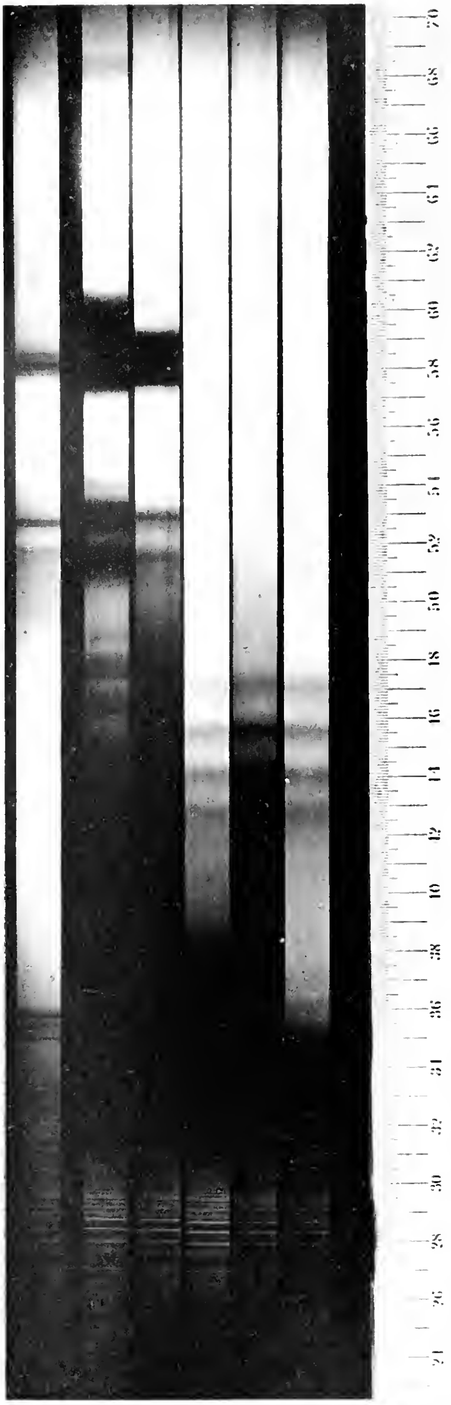

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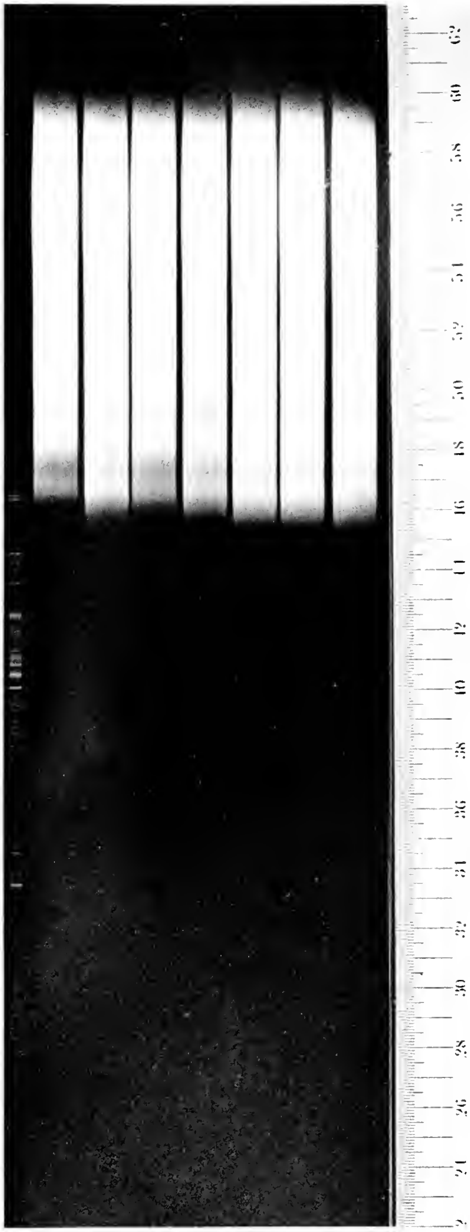
CAMPBELL ART CO., ELIZABETH N. J



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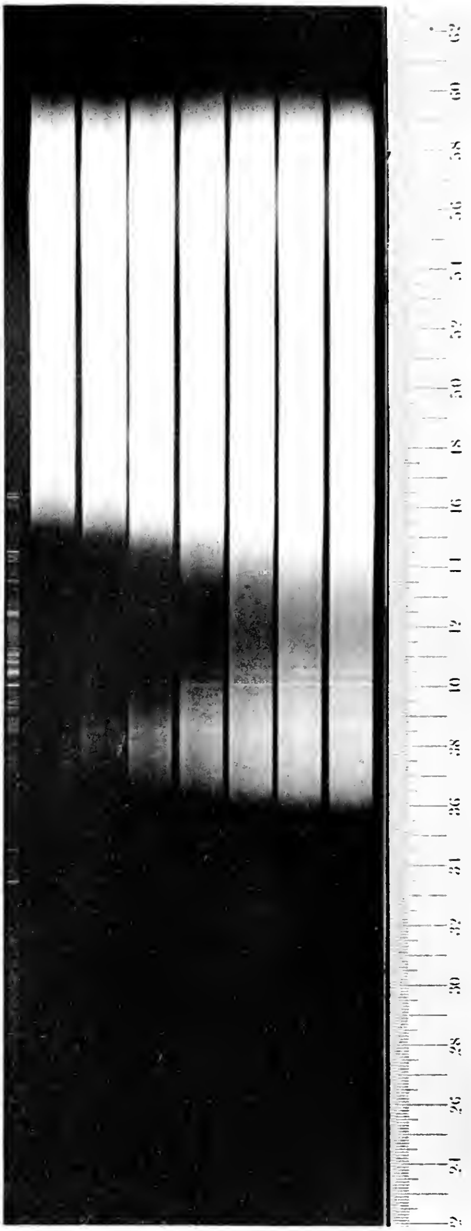

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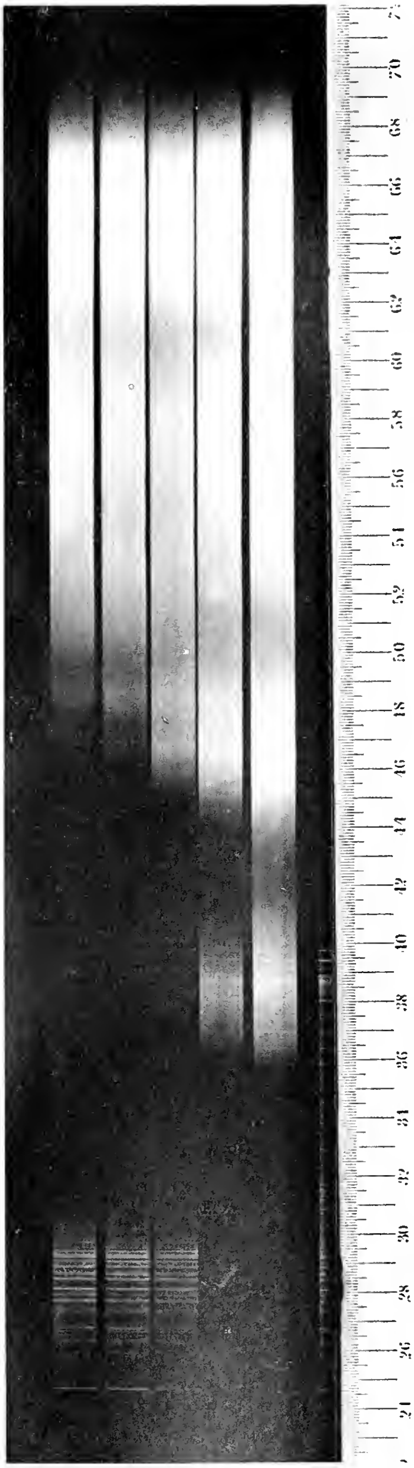
CAMPBELL ART CO., ELIZABETH, N. J.



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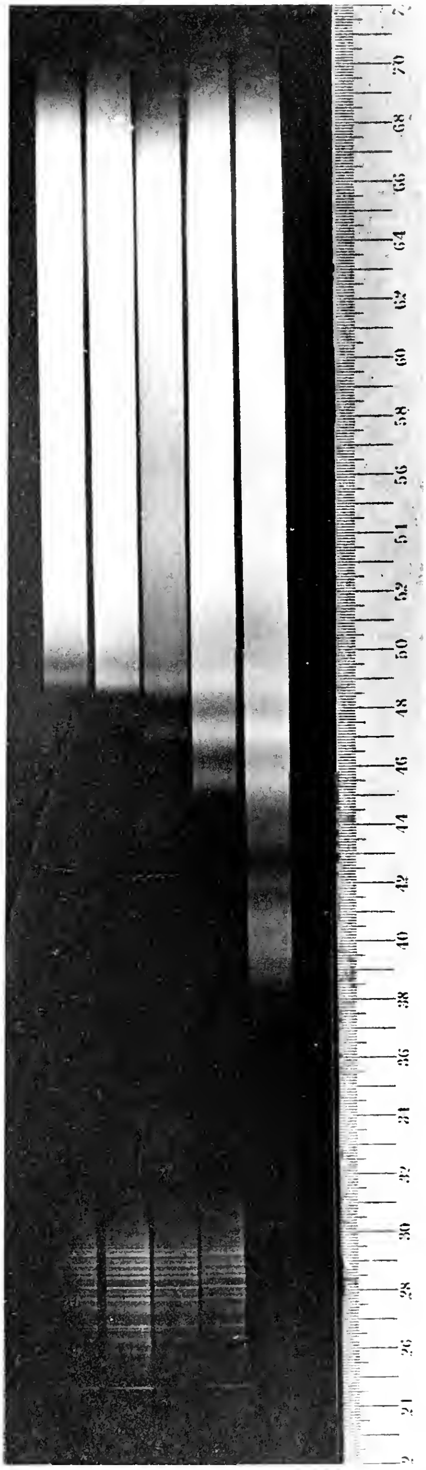
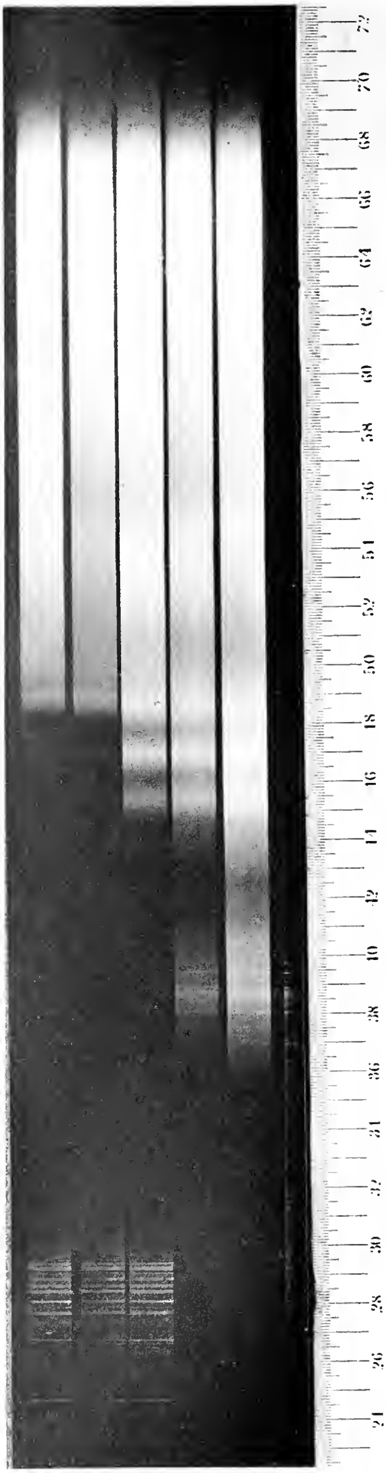


B

CAMPBELL ART CO. ELIZABETH, N.

PLATE 50



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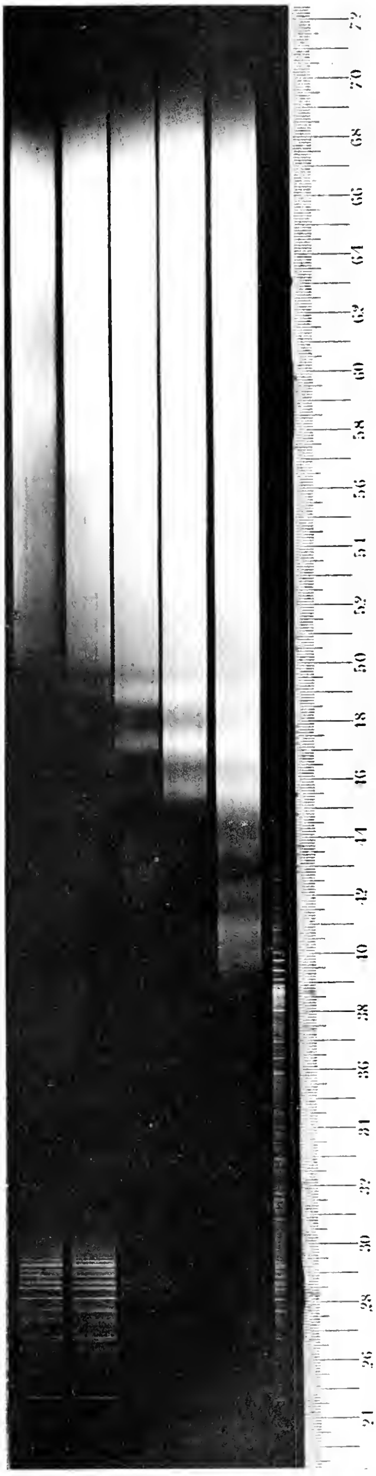

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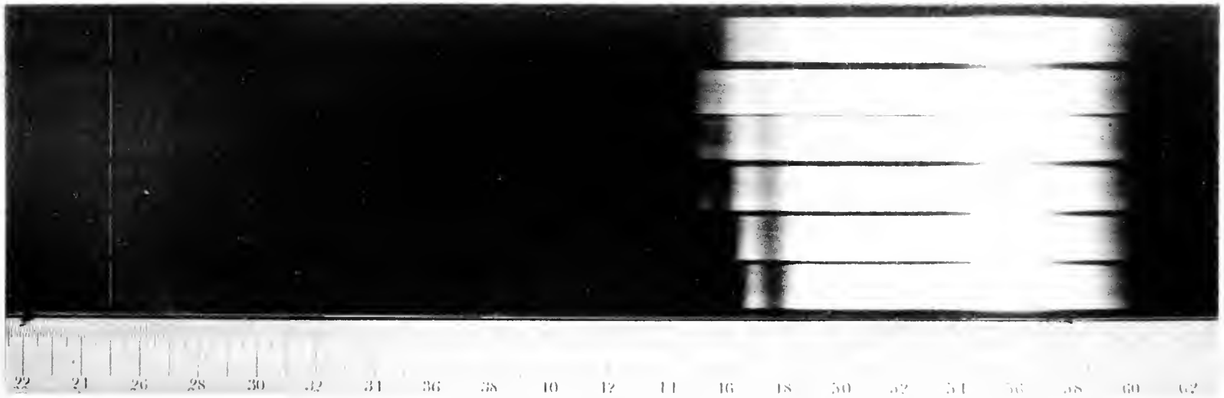
CAMPBELL ART CO., ELIZABETH, N. J



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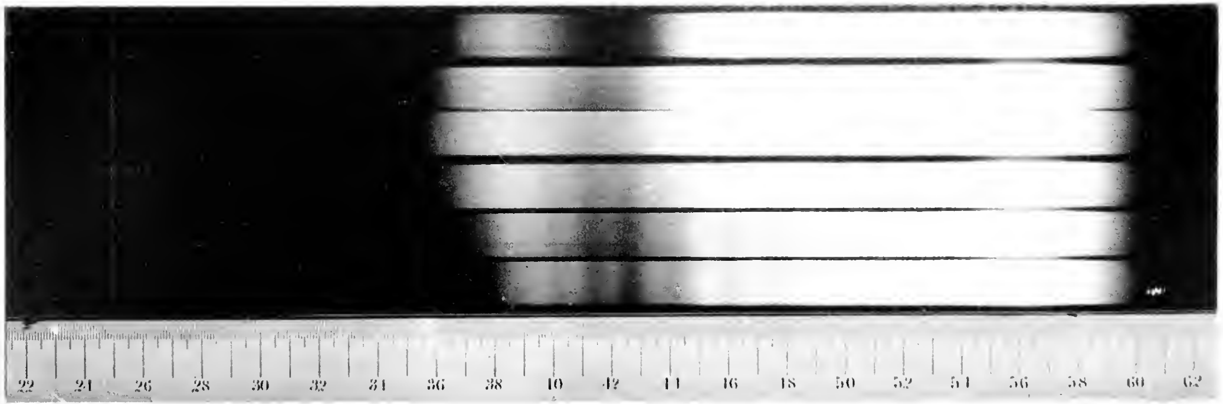

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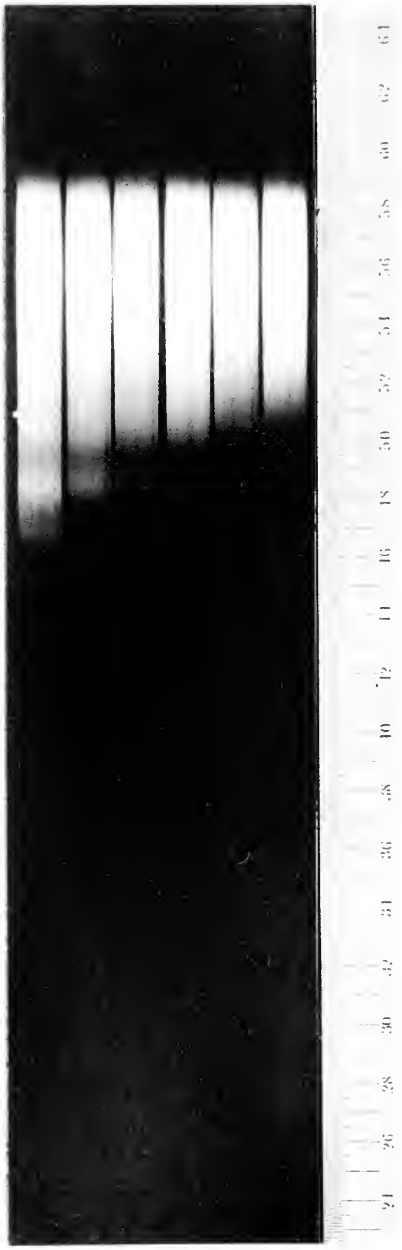
CAMPBELL ART CO., ELIZABETH, N. J.



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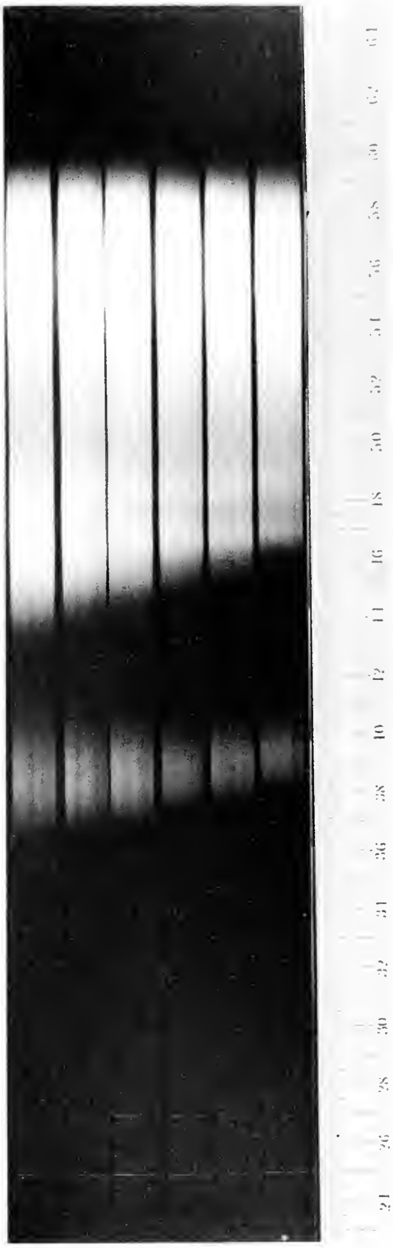

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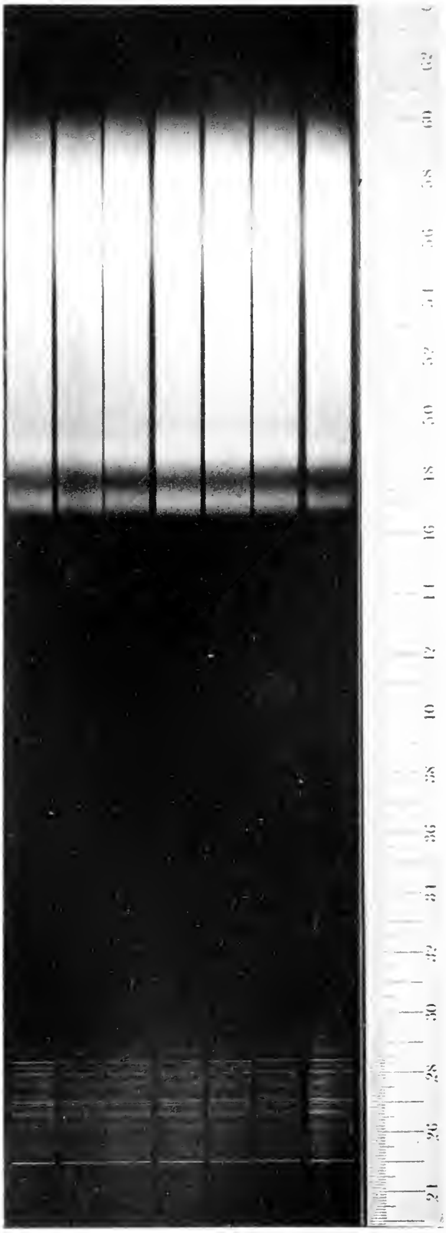
CAMPBELL ART CO., ELIZABETH, N. J



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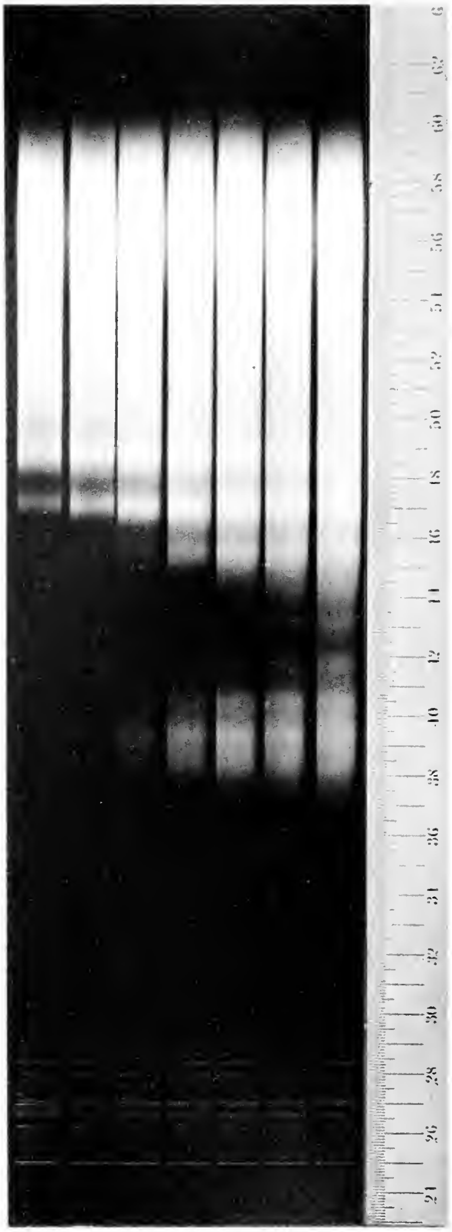

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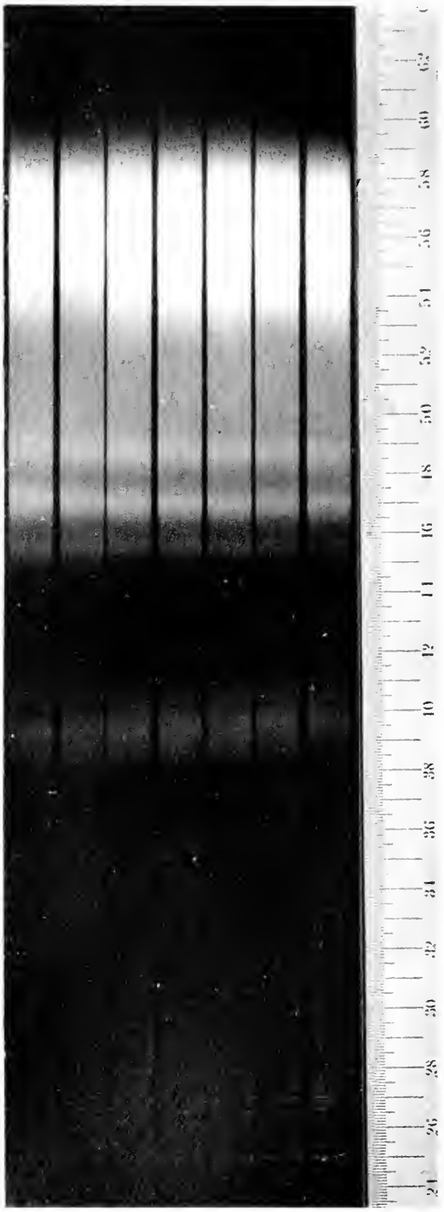
CAMPBELL ART CO., ELIZABETH, N. J.



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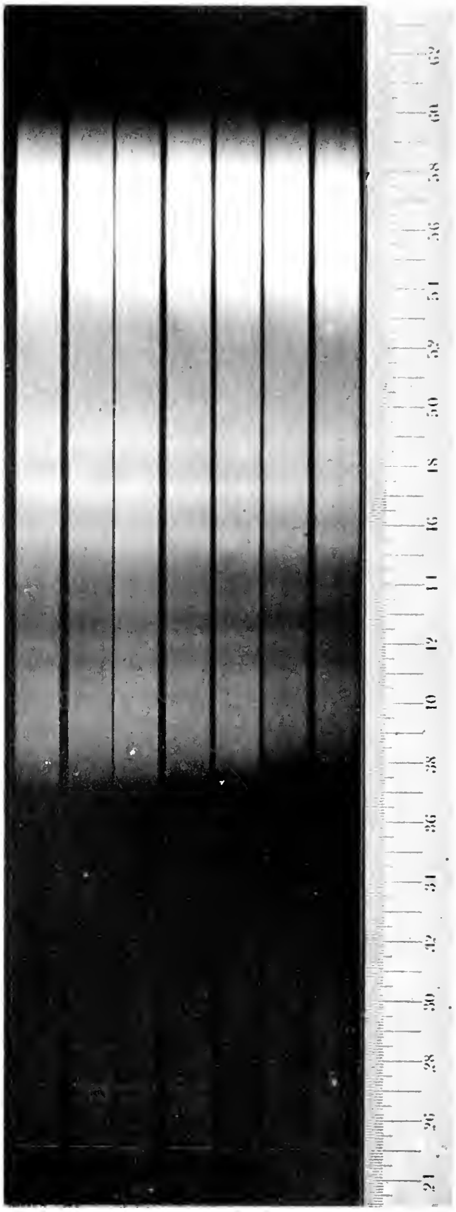

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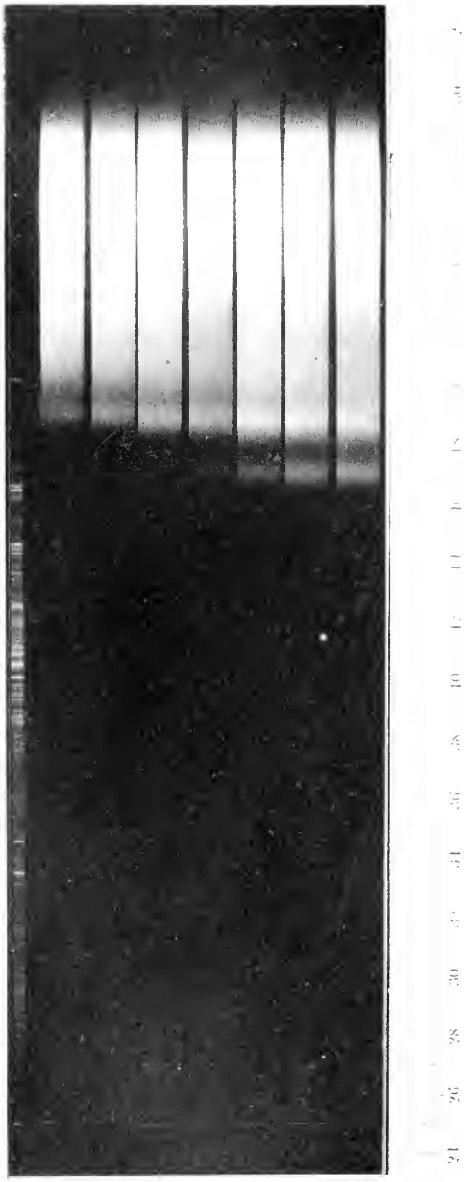
CAMPBELL ART CO., ELIZABETH, N. J.



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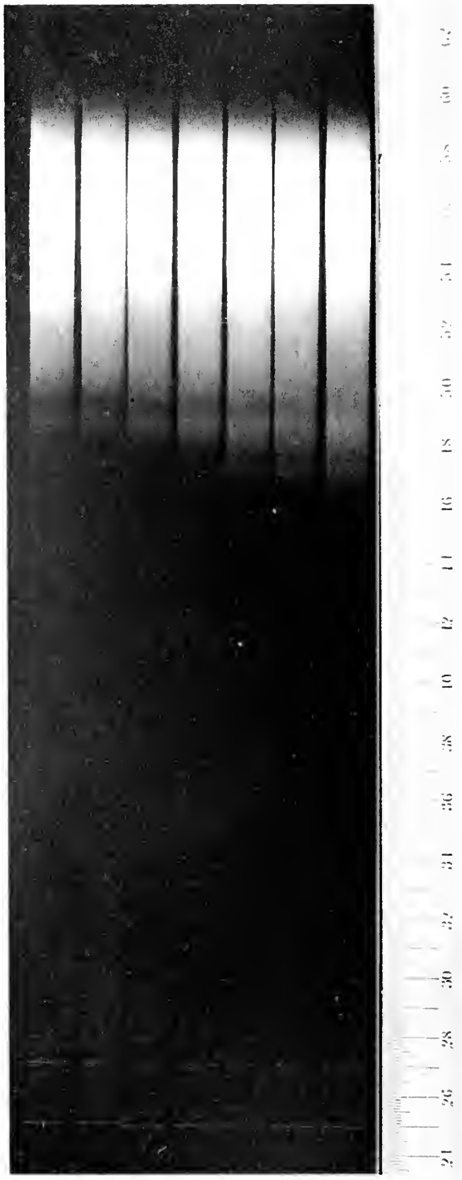

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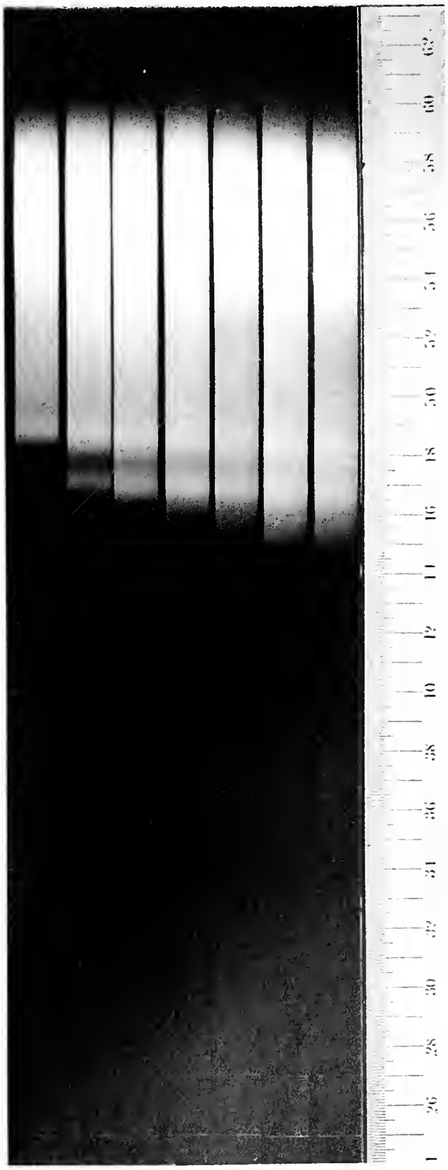
CAMPBELL ART CO., ELIZABETH, N. J.



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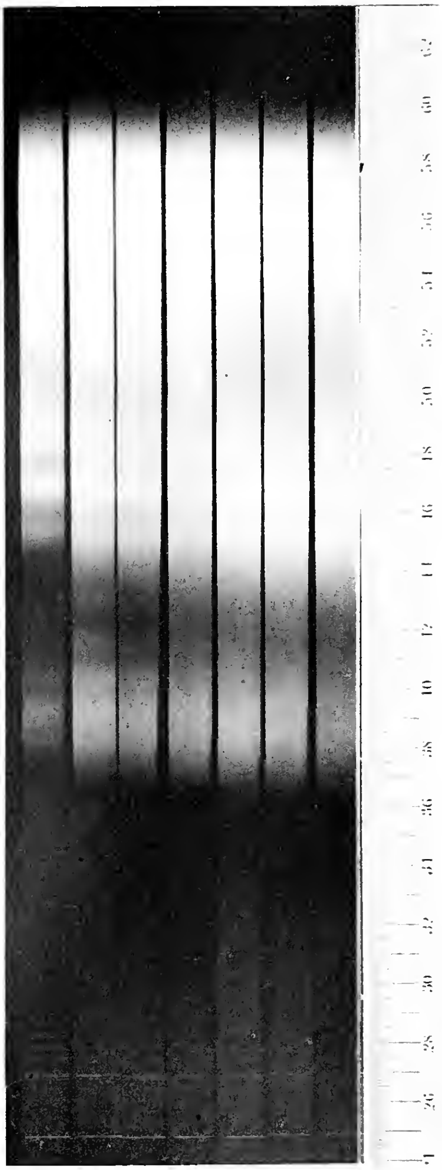

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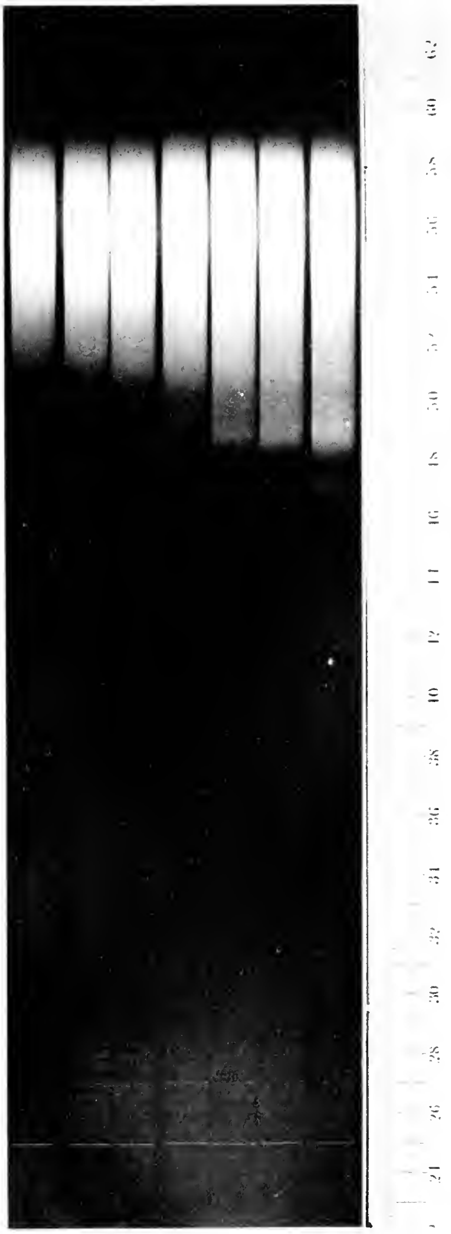
CAMPBELL ART CO., ELIZABETH, N



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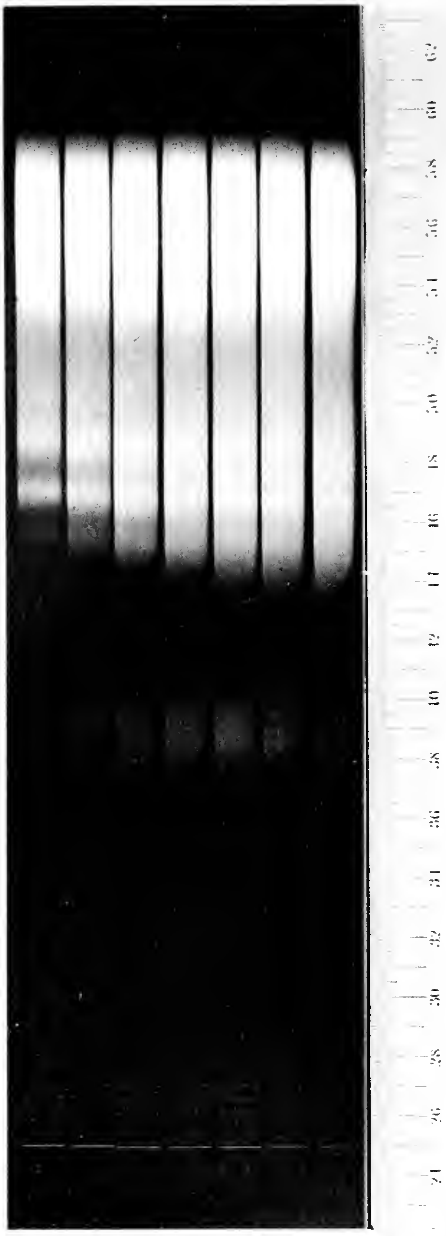

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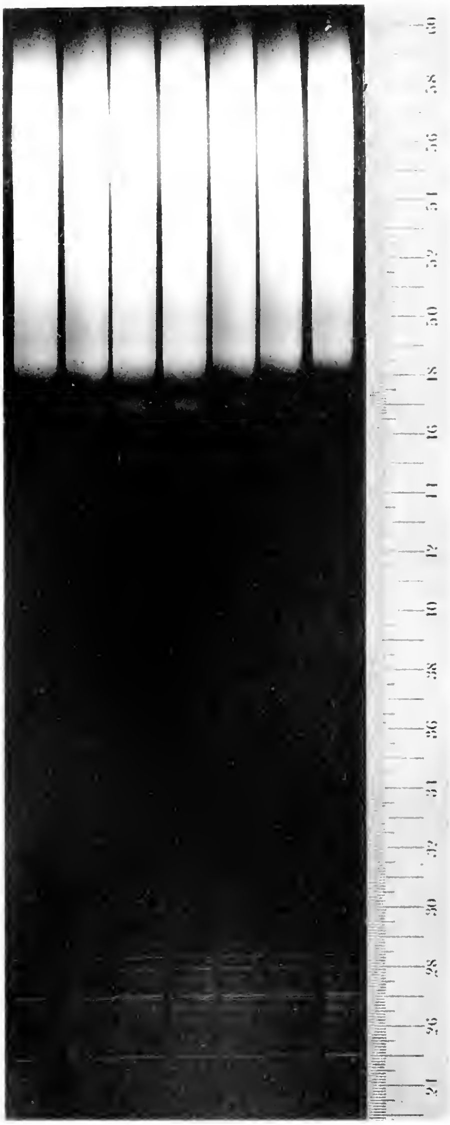
CAMPBELL ART CO., ELIZABETH N. J.



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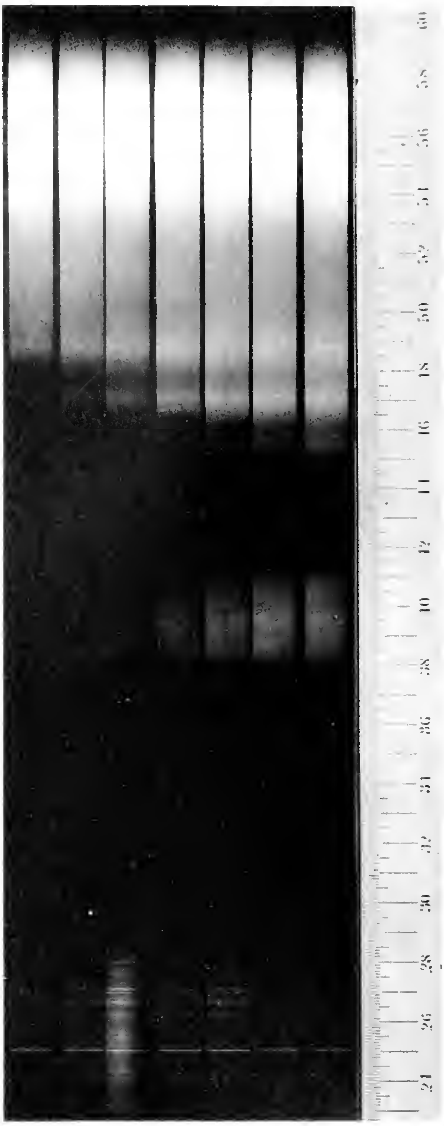

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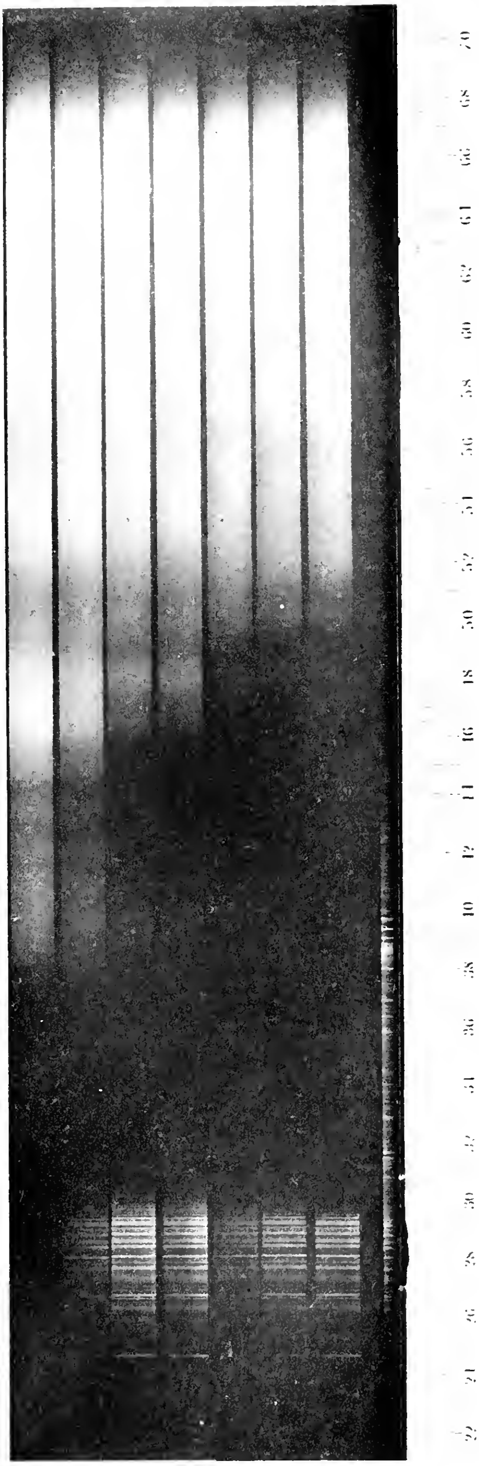
CAMPBELL ART CO., ELIZABETH, N



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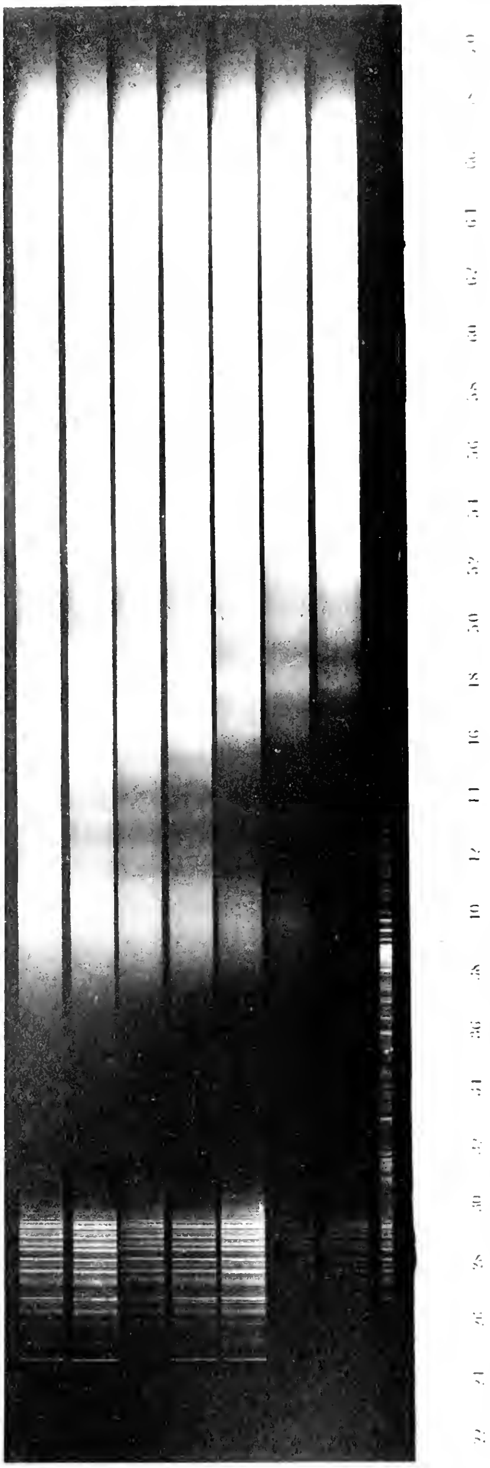

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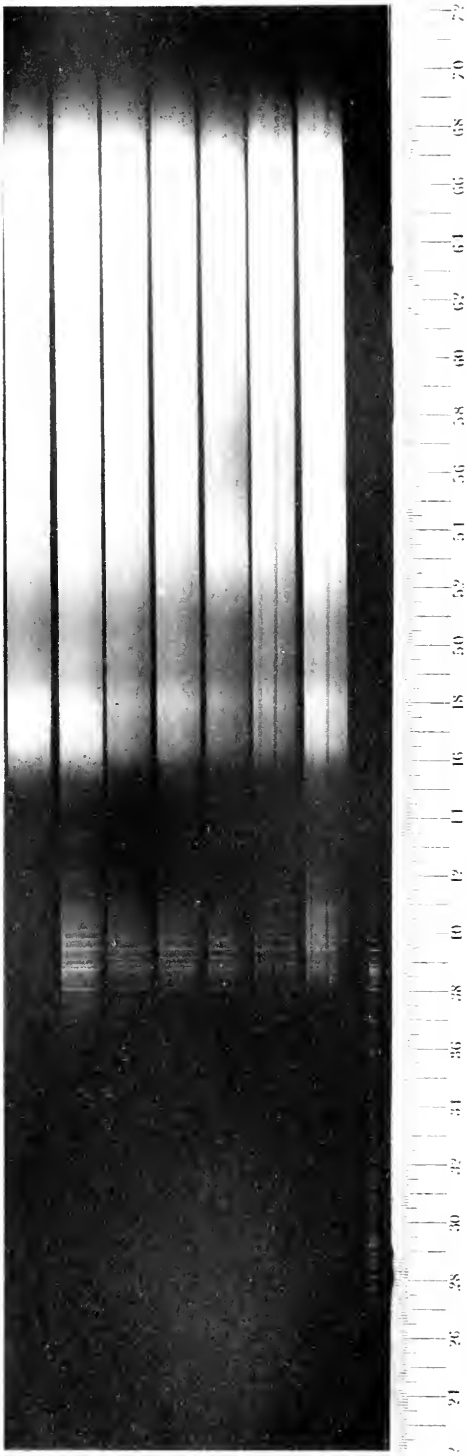
CAMPBELL ART CO., ELIZABETH, N.



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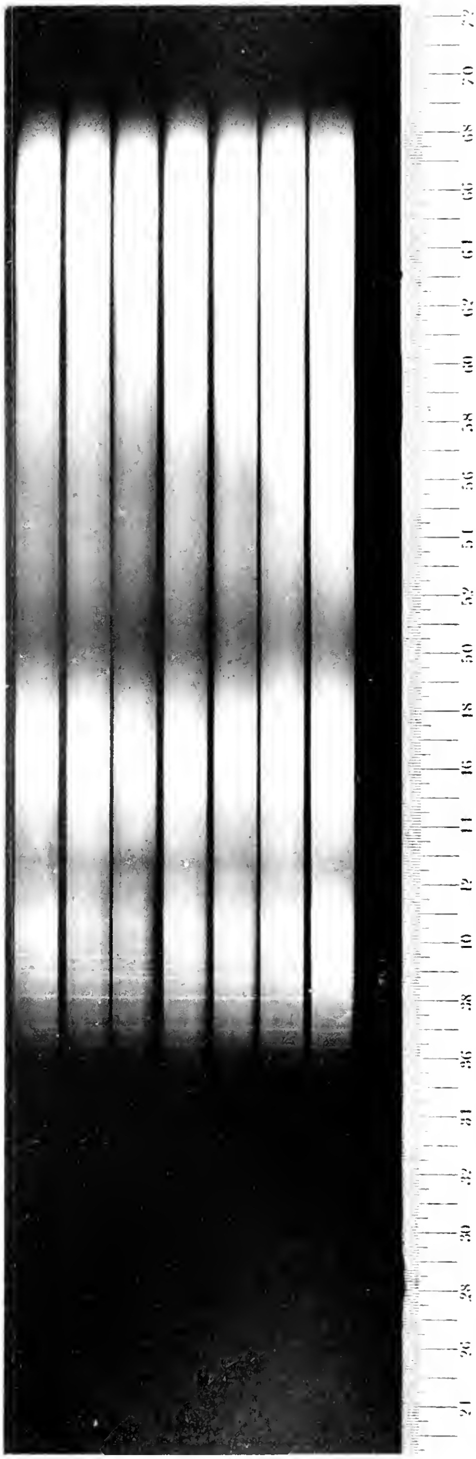

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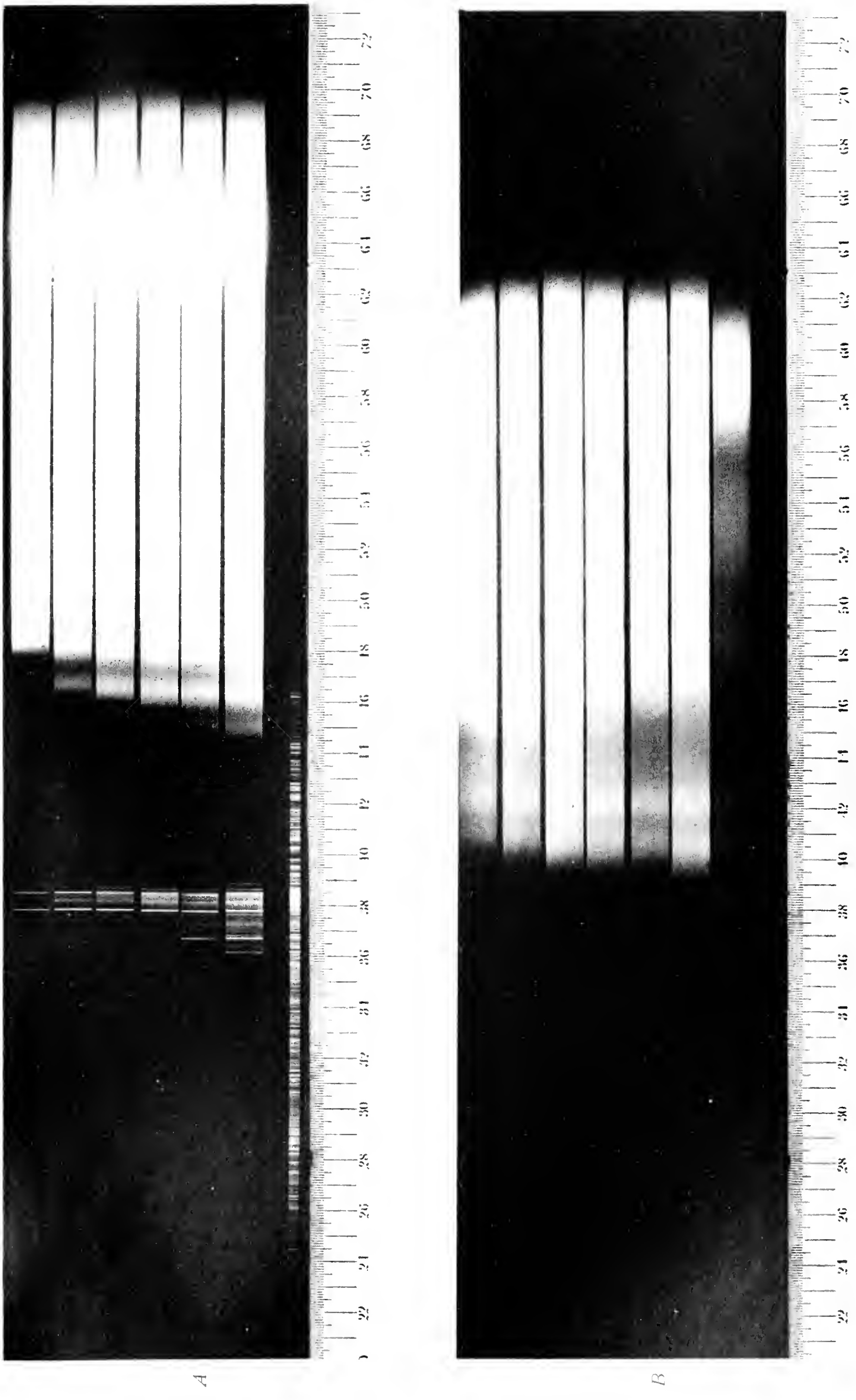
AMPBELL ART CO., ELIZABETH, N. J

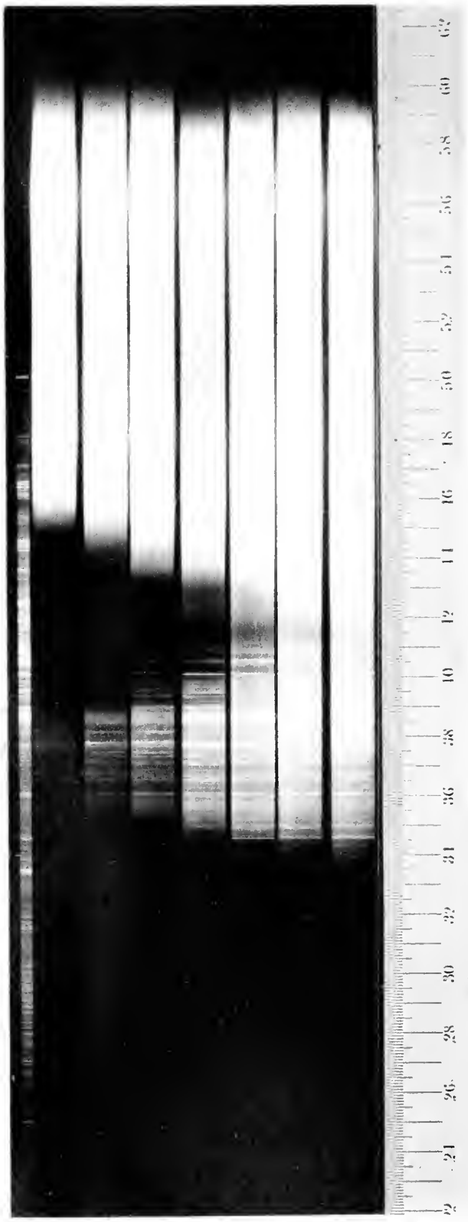


A

B

CAMPBELL ART CO., ELIZABETH, N. J.

PLATE 62



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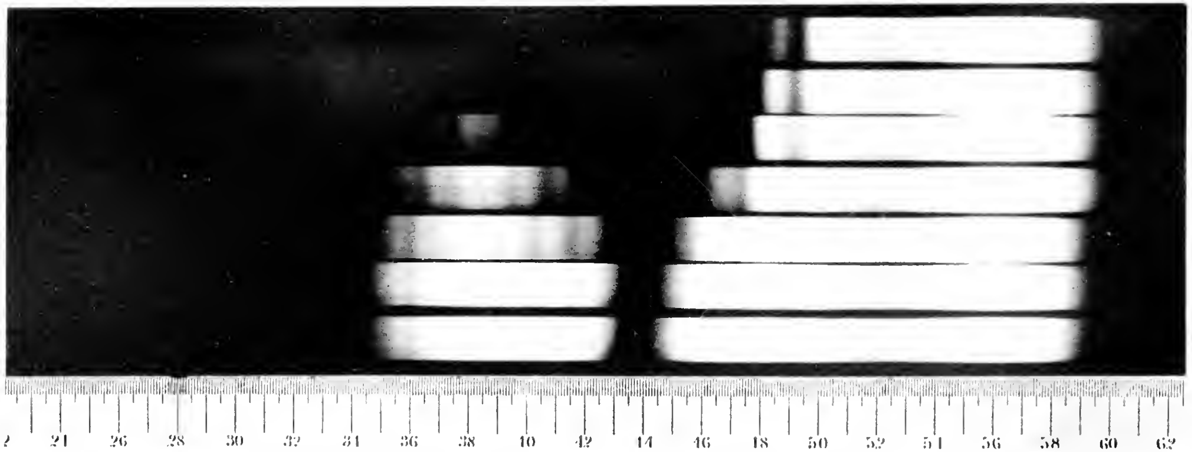
CAMPBELL ART CO., ELIZABETH, N. J.

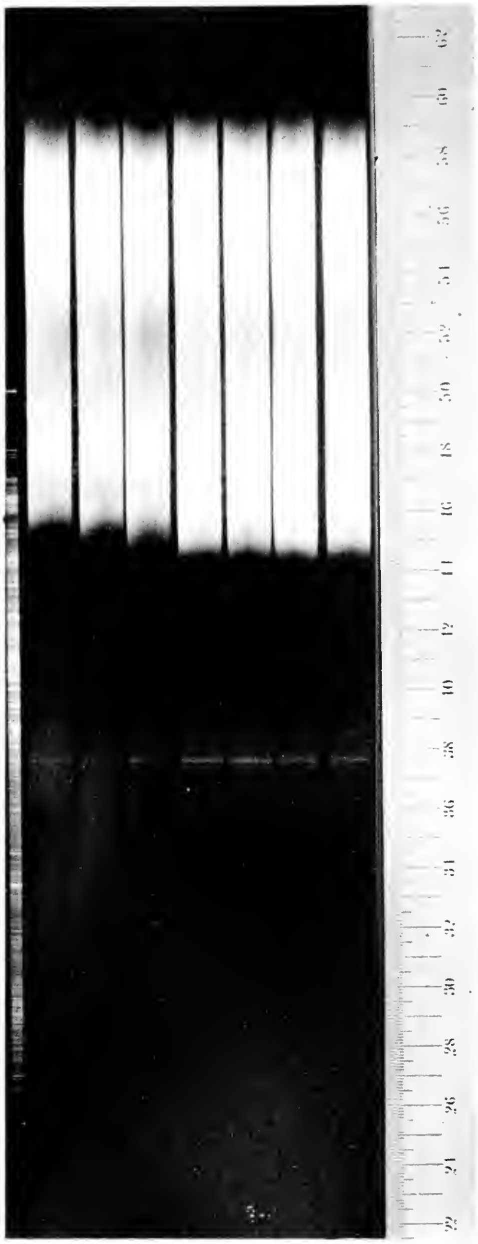


A

B

CAMPBELL ART CO., ELIZABETH, N. J.

PLATE 64



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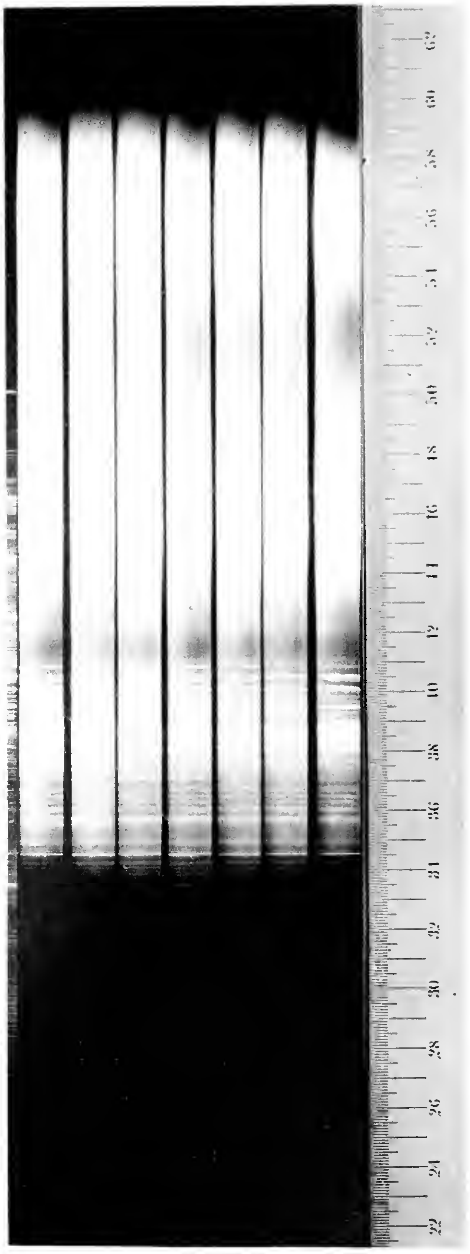

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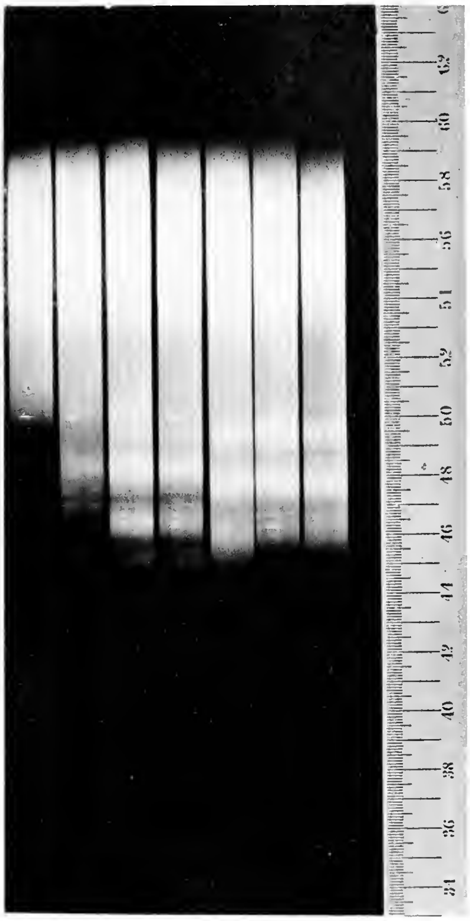
CAMPBELL ART CO., ELIZABETH, N. J.



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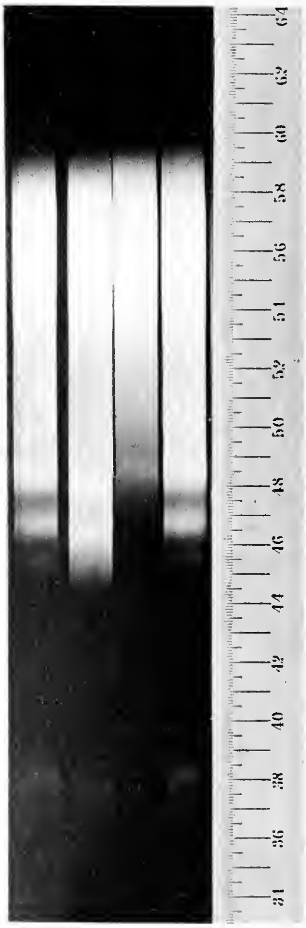

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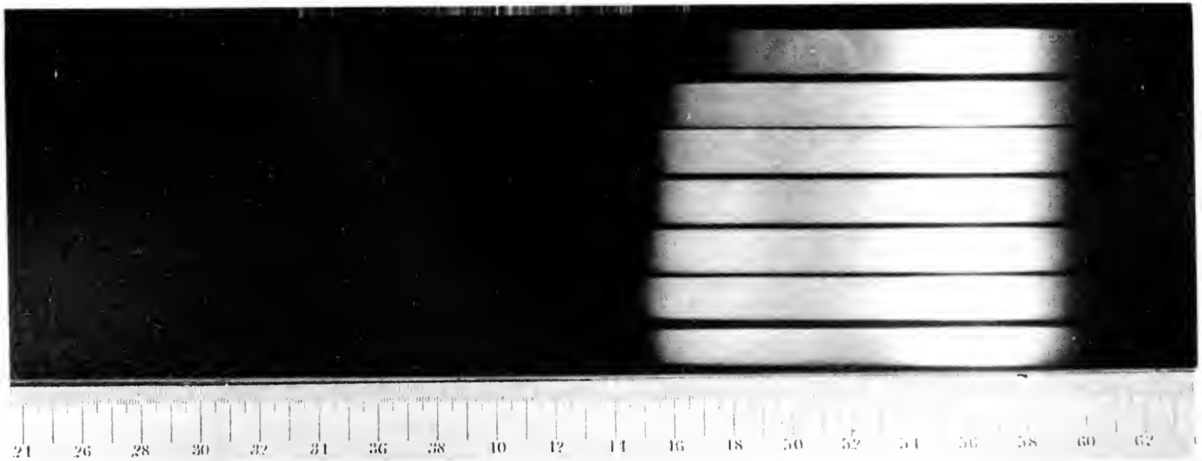
CAMPBELL ART CO., ELIZABETH, N. J.

A



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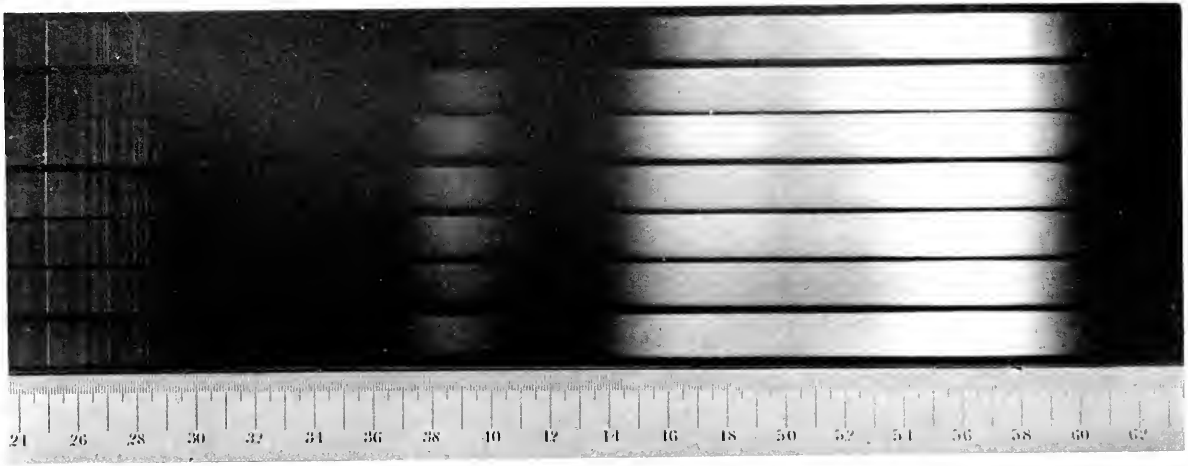
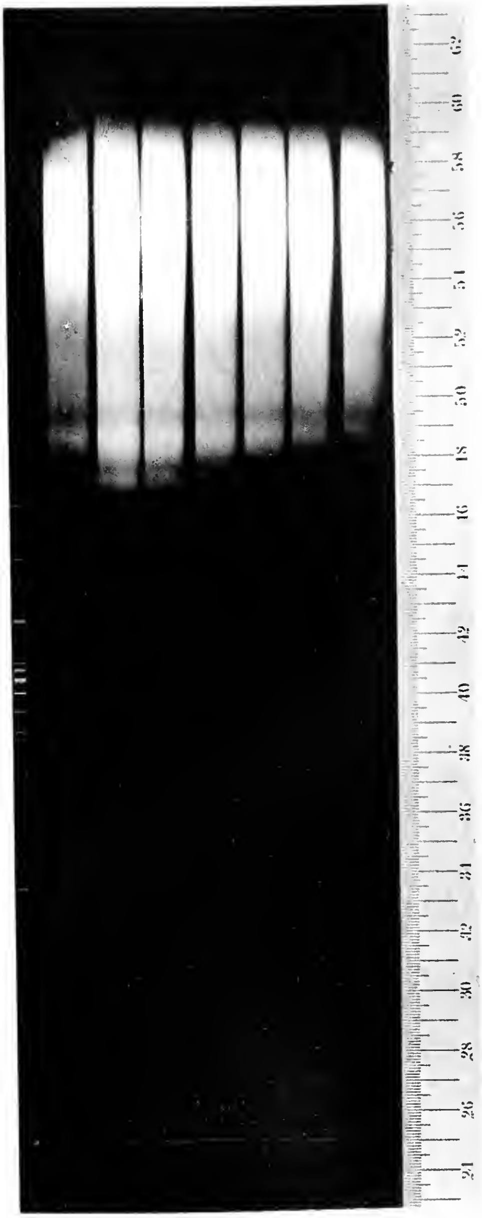


CAMPBELL ART CO. ELIZABETH, N



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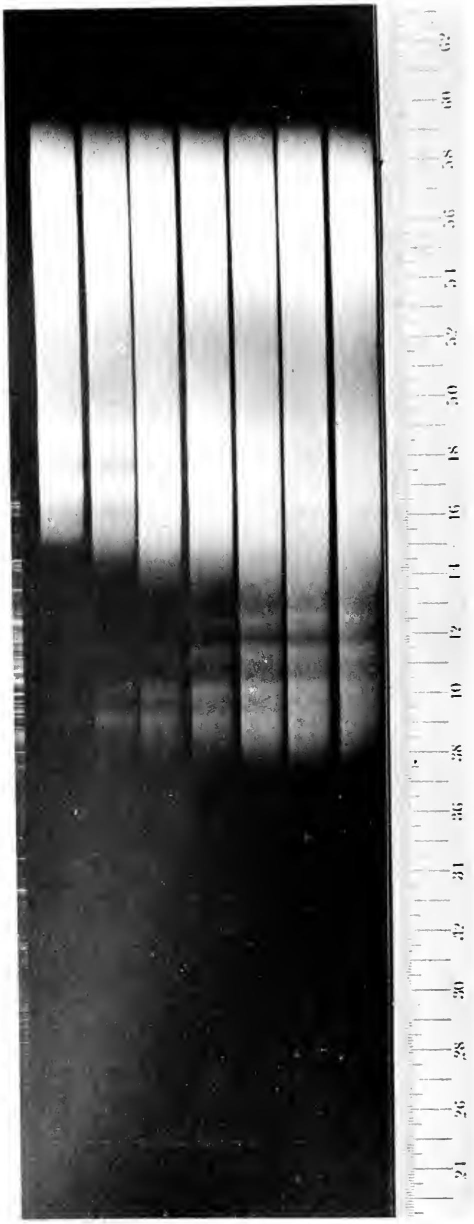

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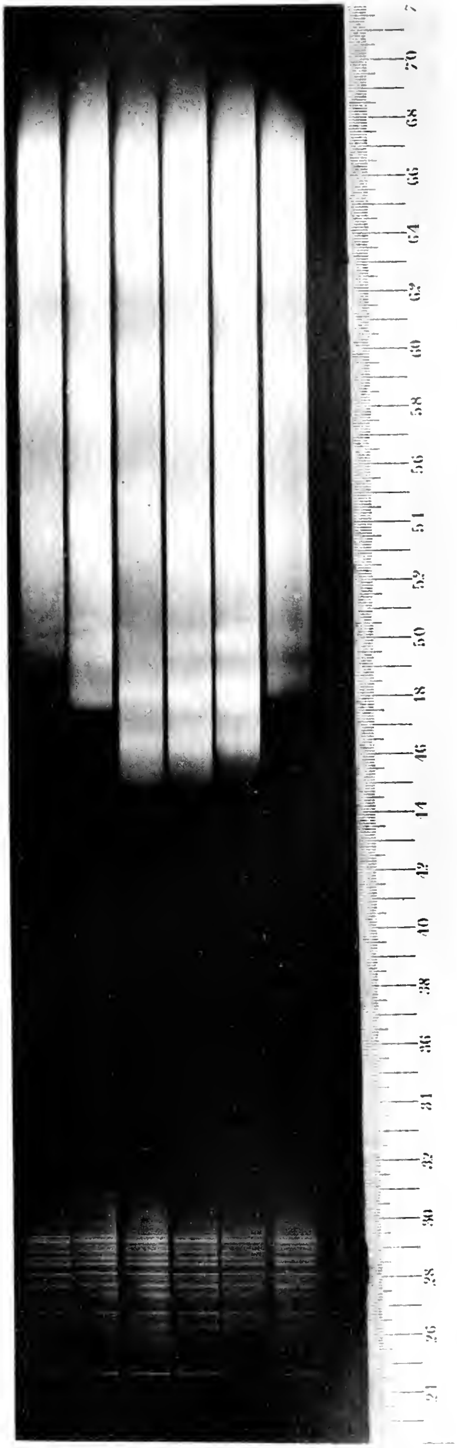
CAMPBELL ART CO., ELIZABETH N. J

PLATE 69



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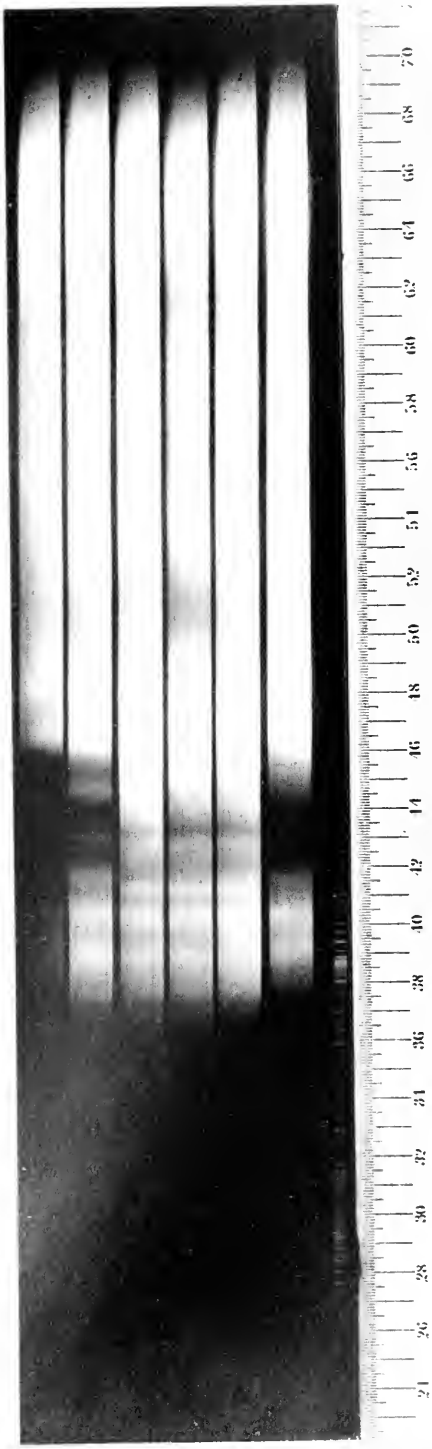

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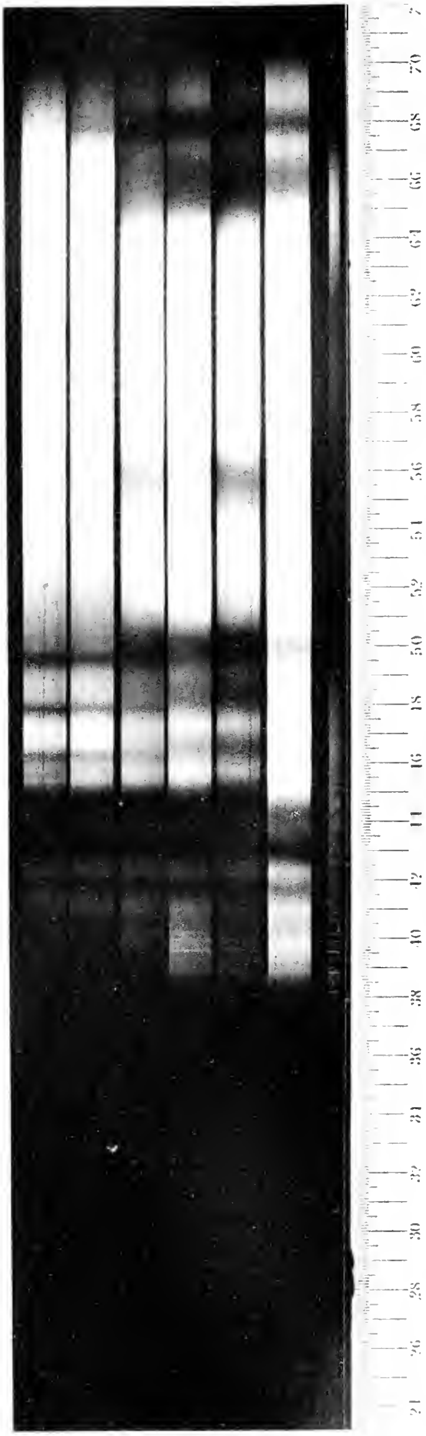
CAMPBELL ART CO., ELIZABETH, N. J.



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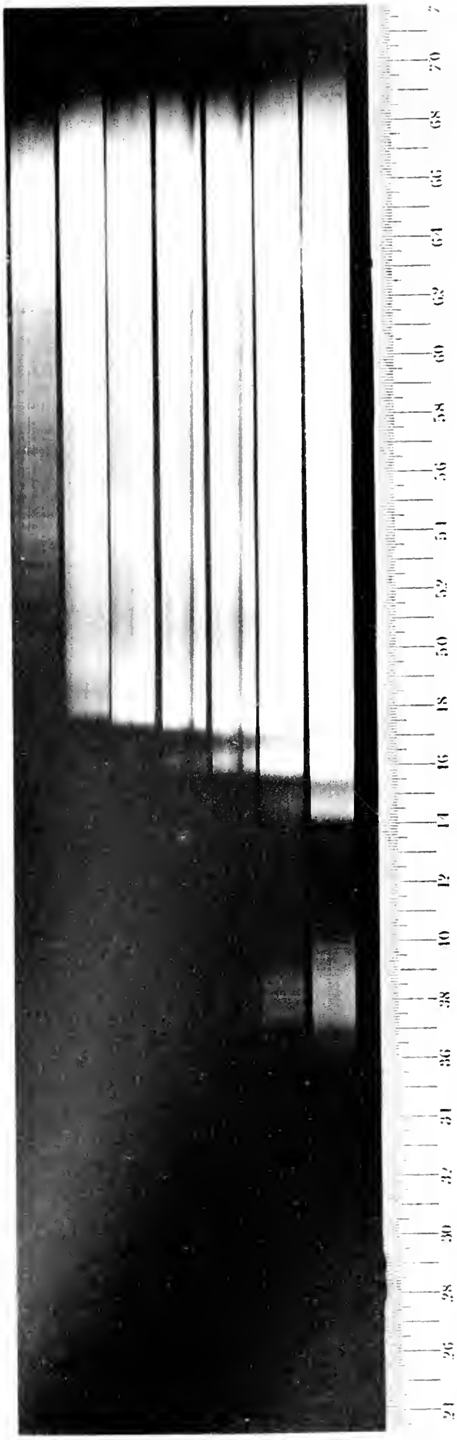

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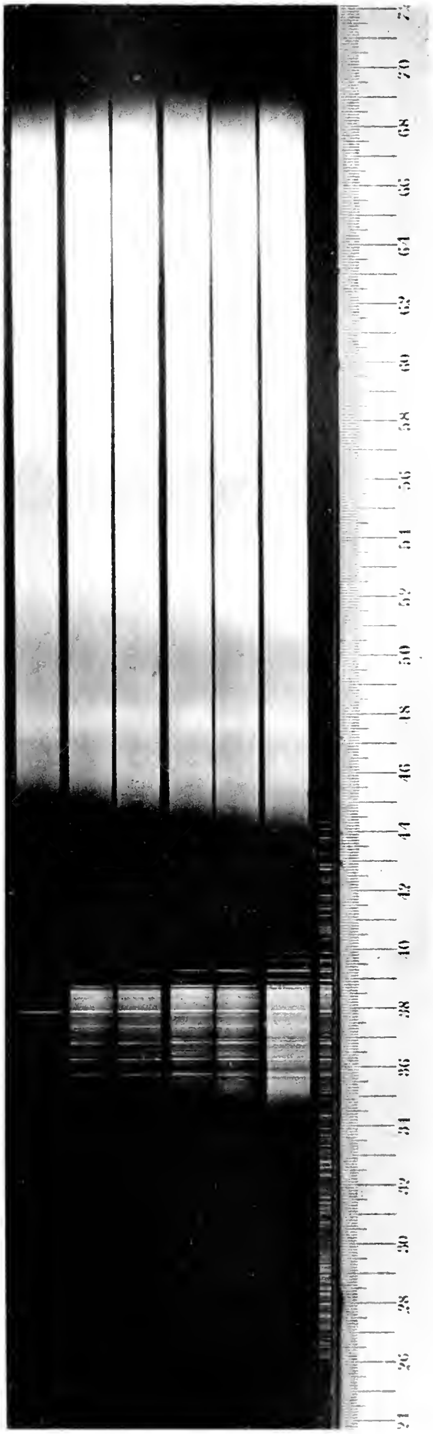
CAMPBELL ART CO., ELIZABETH, N. J



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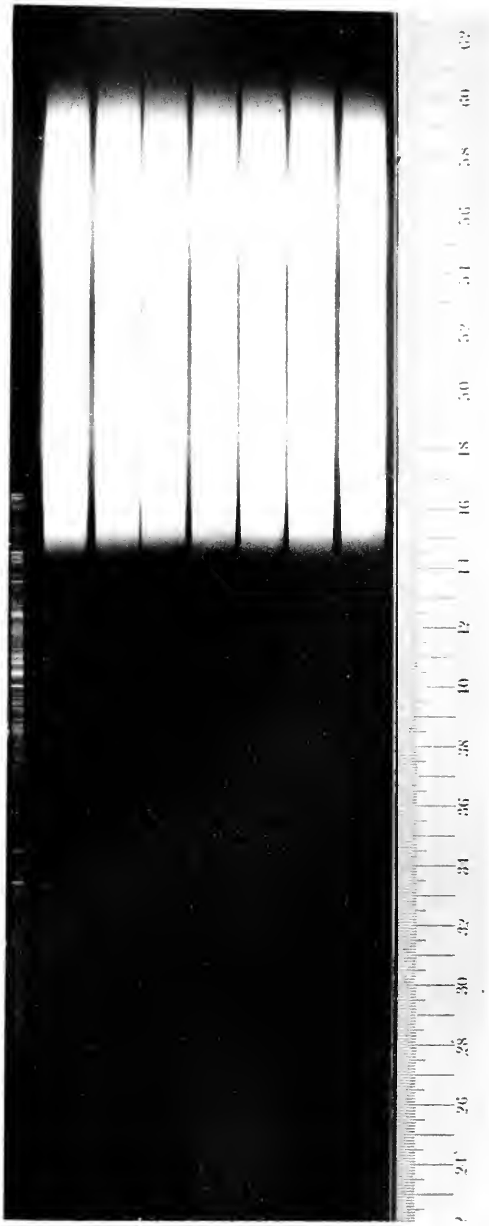
CAMPBELL ART CO., ELIZABETH, N. J.



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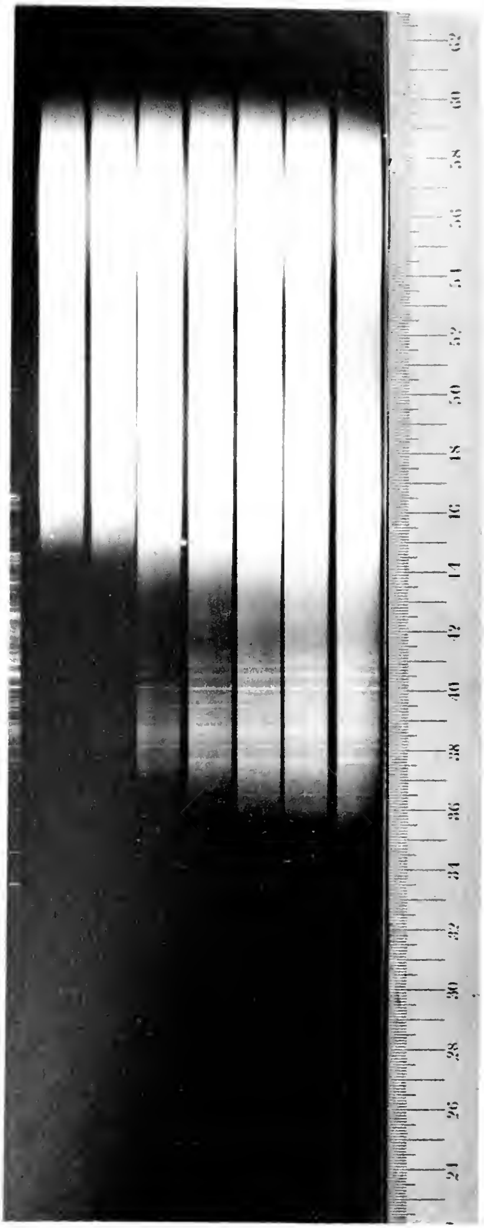

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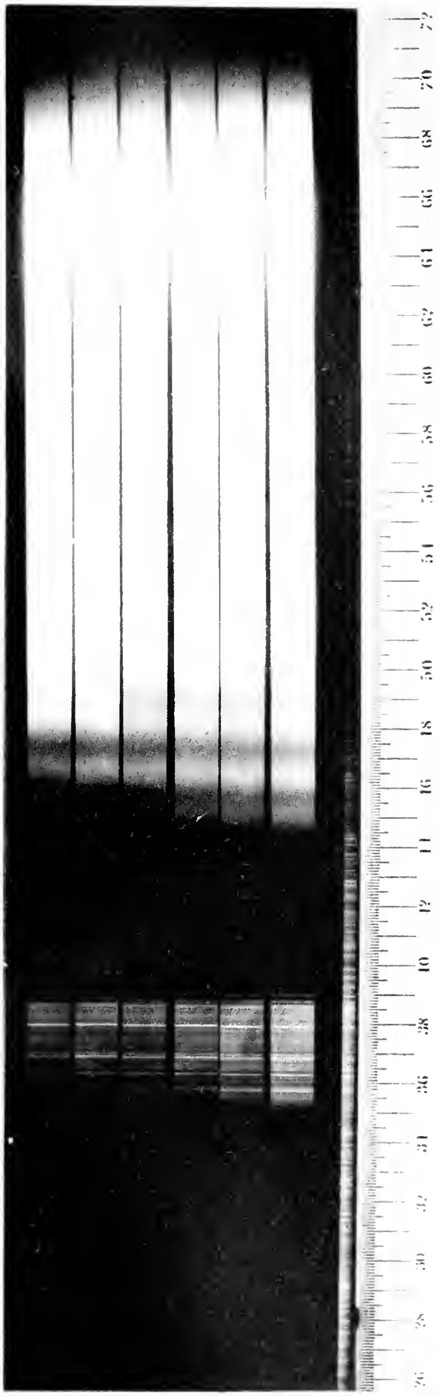
CAMPBELL ART CO., ELIZABETH, N. J



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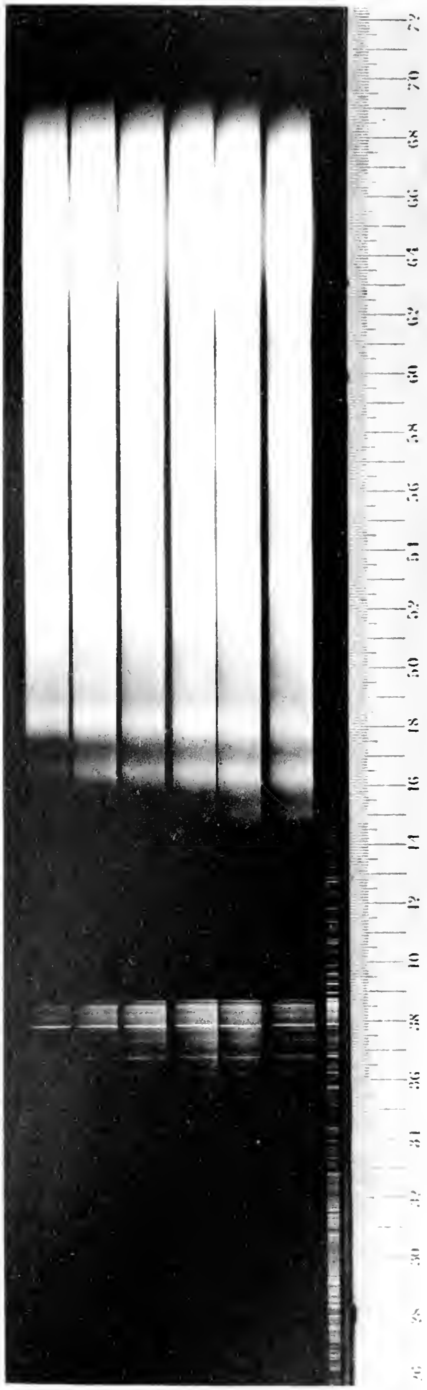

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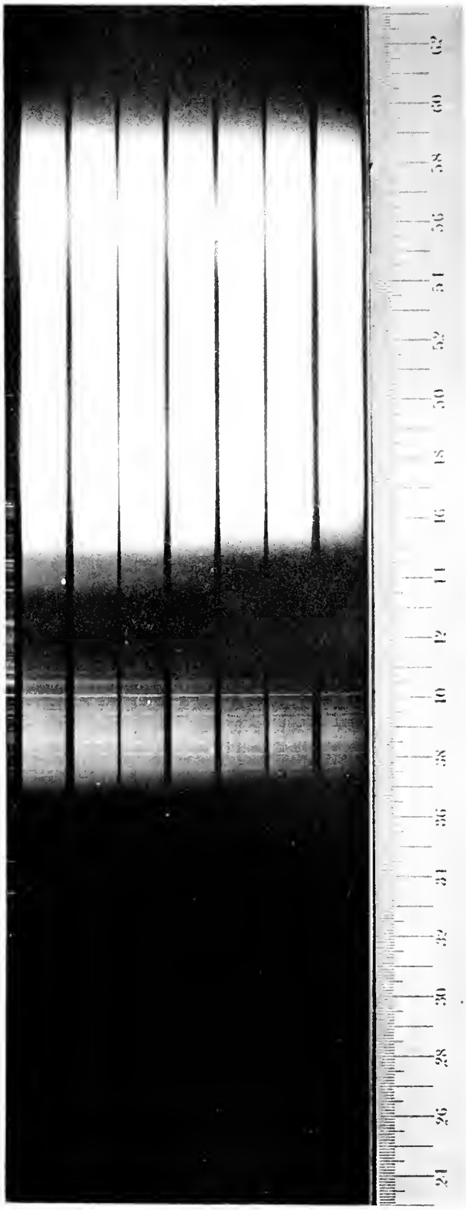
CAMPBELL ART CO., ELIZABETH, N. J.



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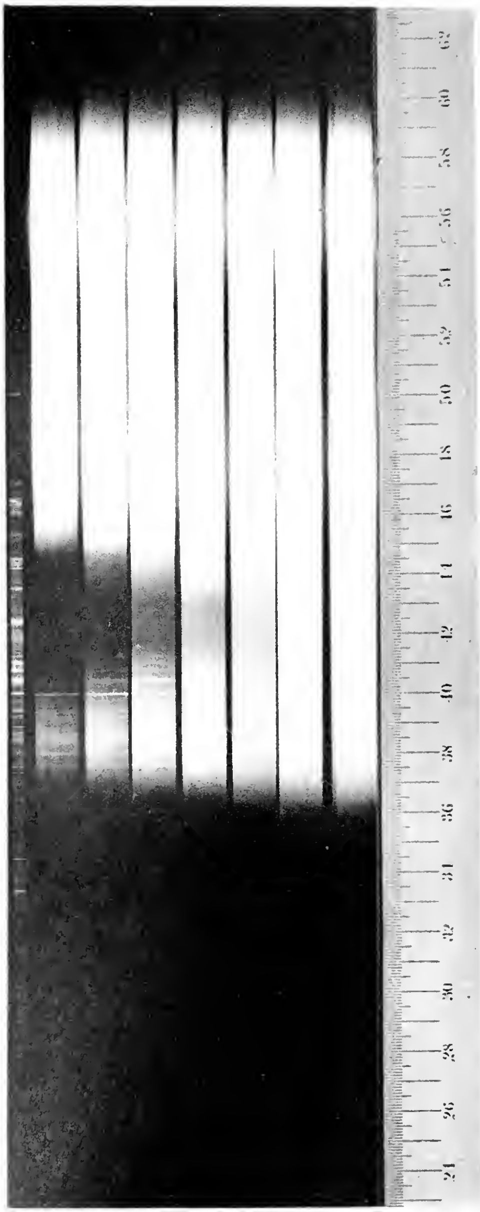
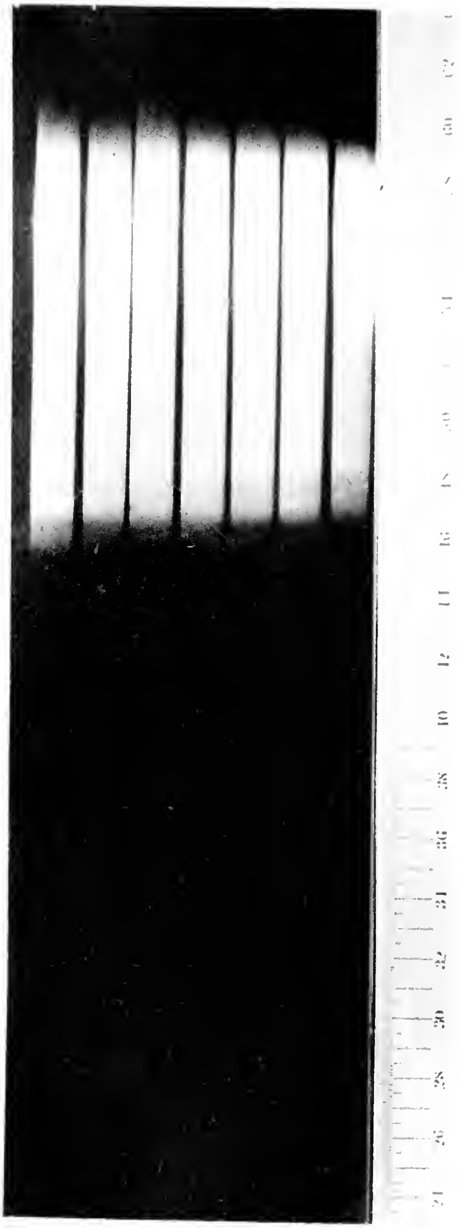


B

CAMPBELL ART CO., ELIZABETH, N. J.

PLATE 75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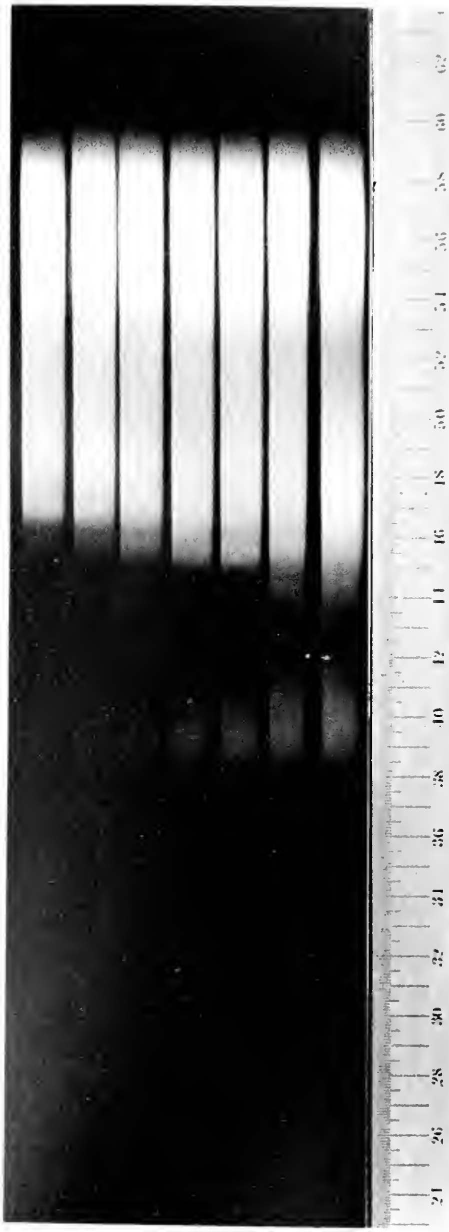
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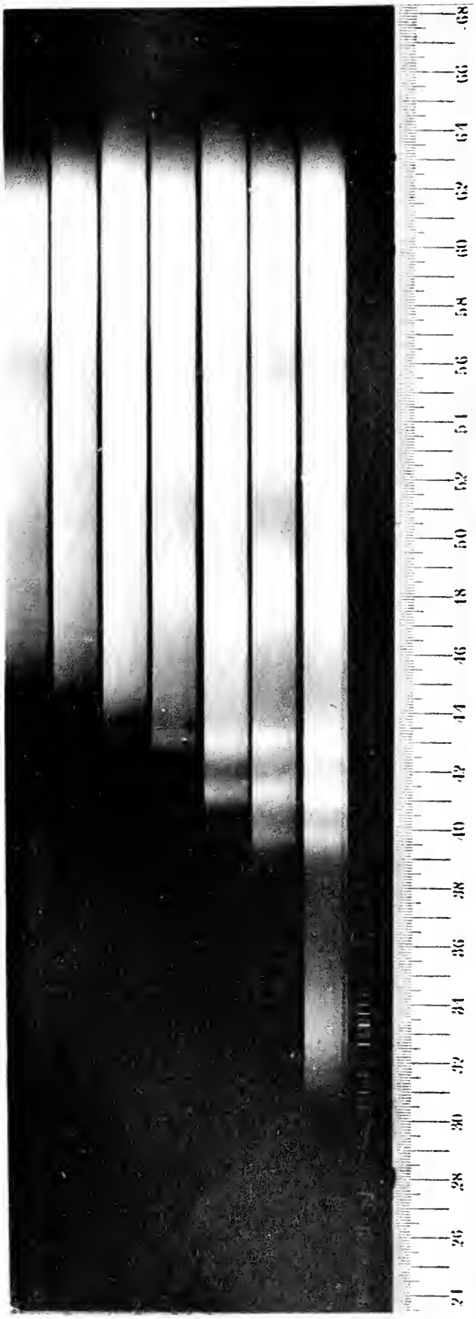
CAMPBELL ART CO., ELIZABETH, N. J.



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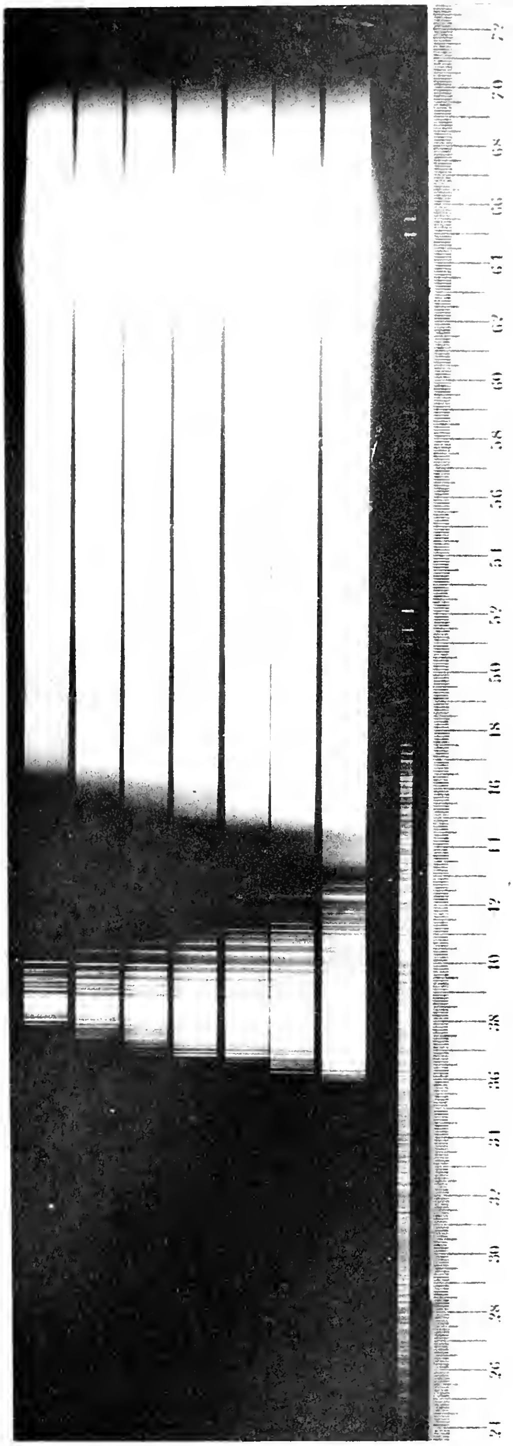
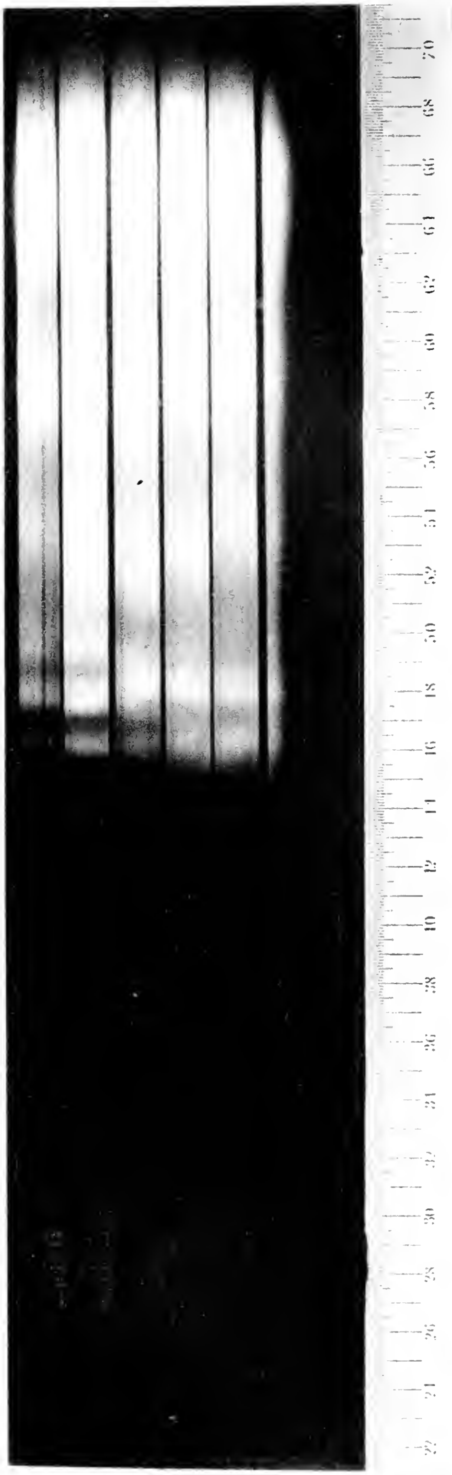


B

CAMPBELL ART CO ELIZABETH, N J

PLATE 77



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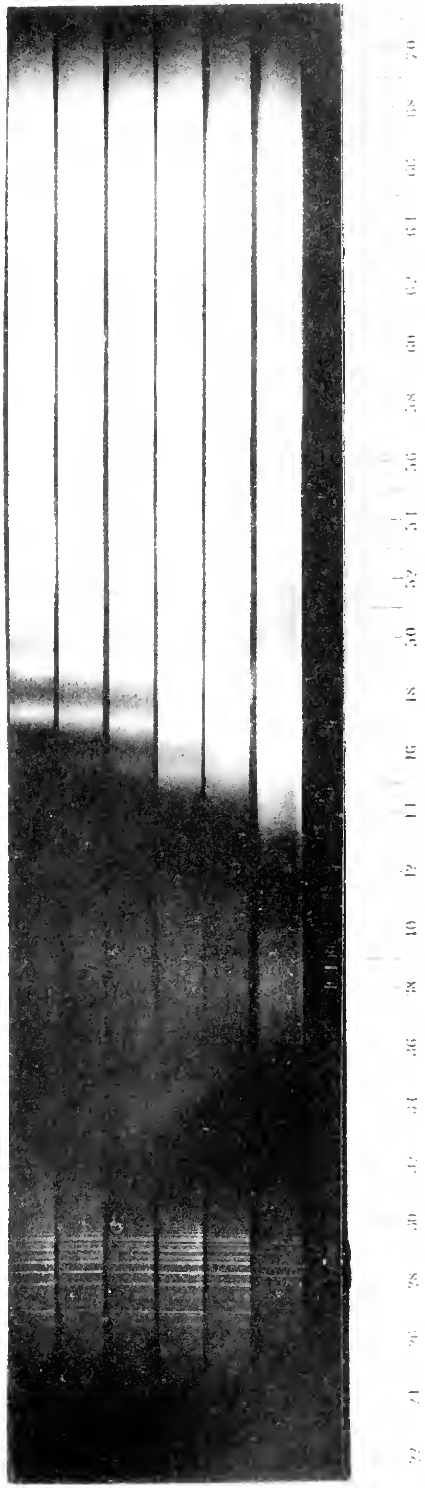
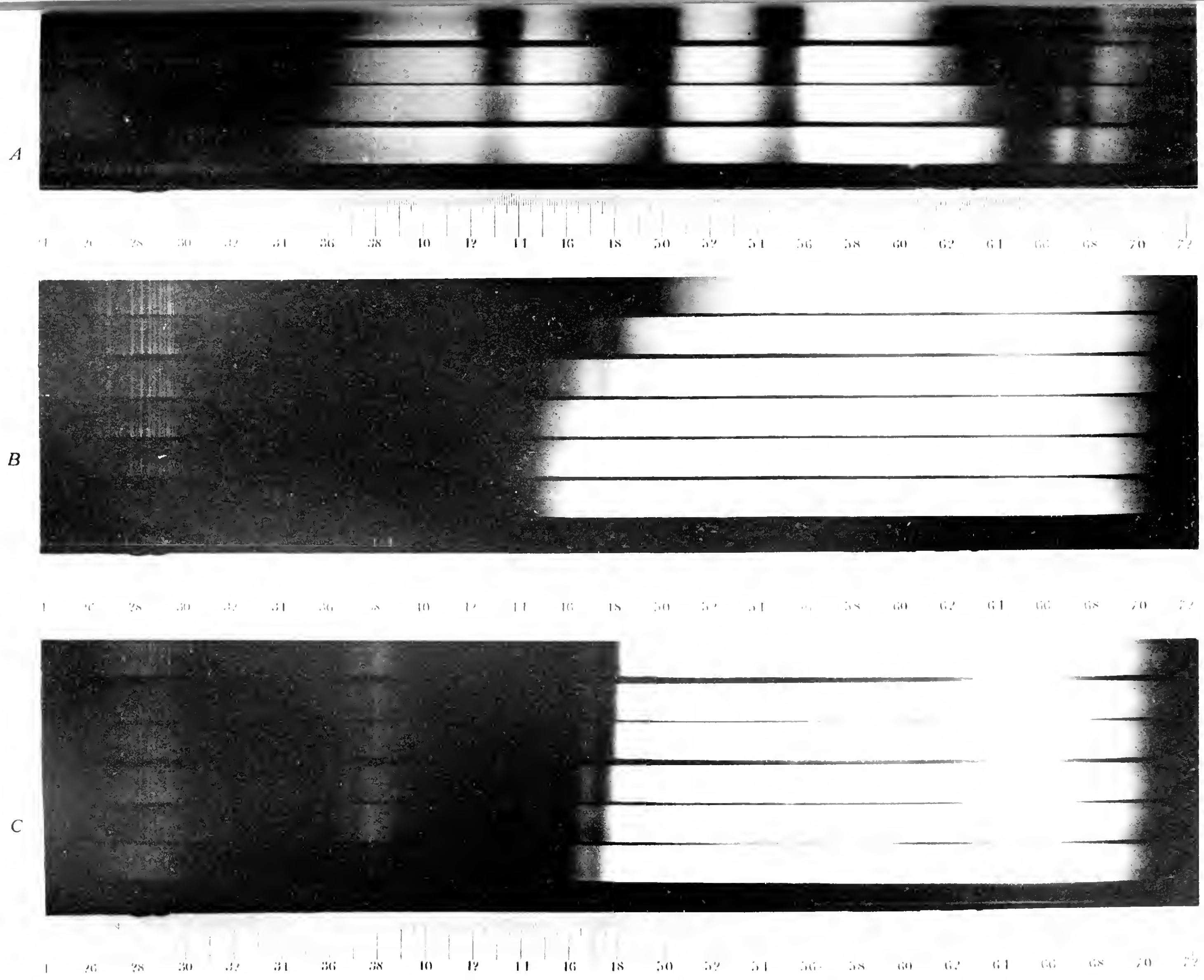
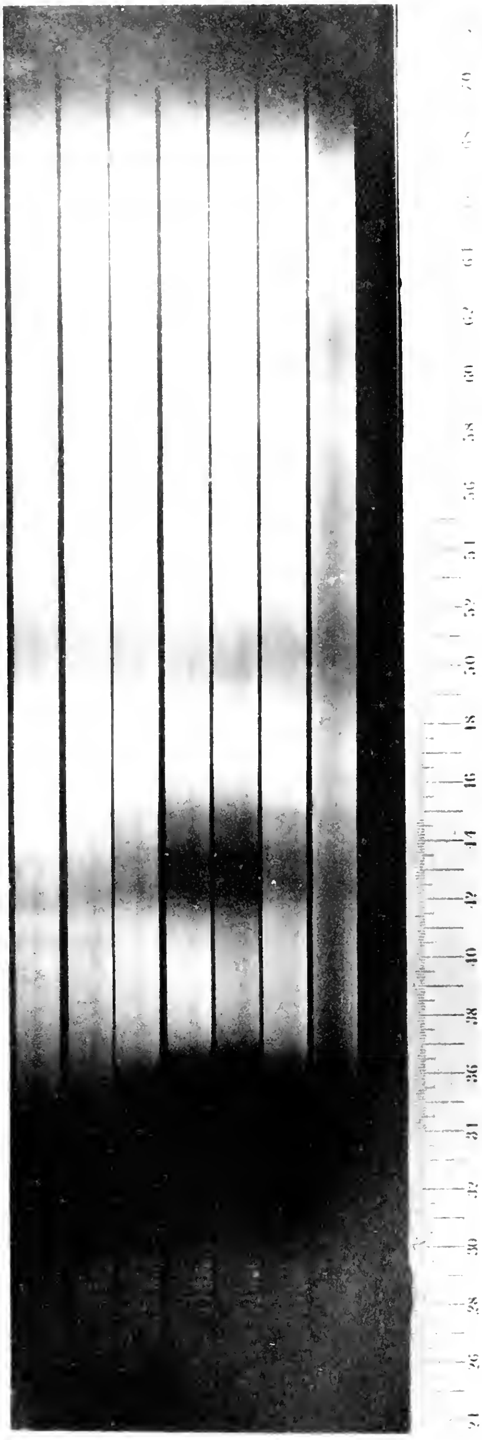


B

CAMPBELL ART CO., ELIZABETH, N. J.

CAMPBELL ART CO., ELIZABETH, N. J.





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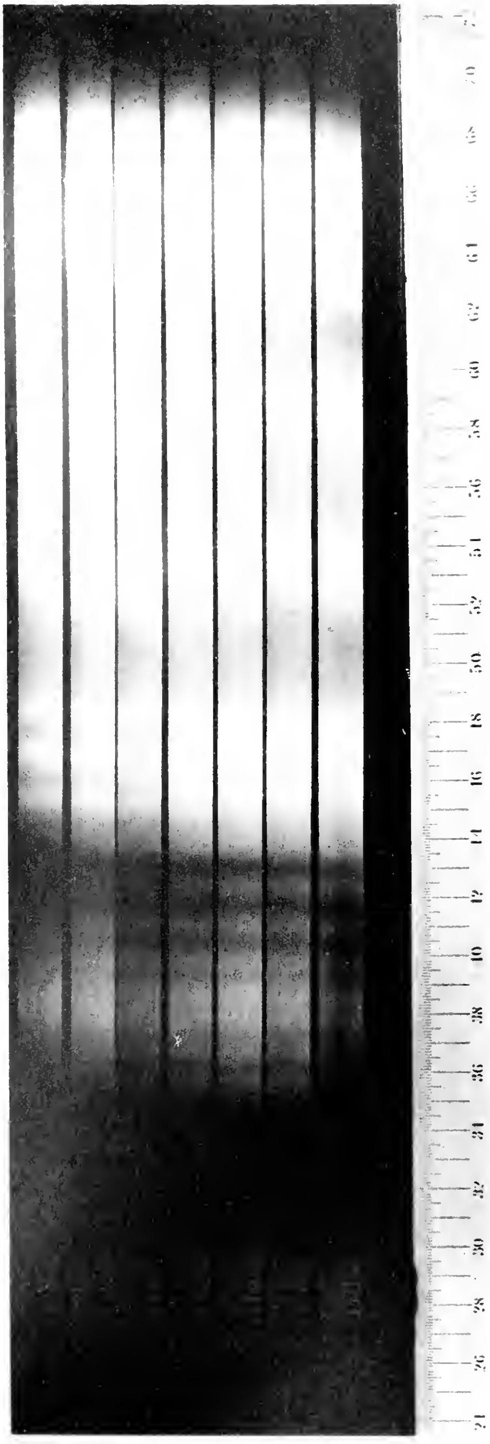
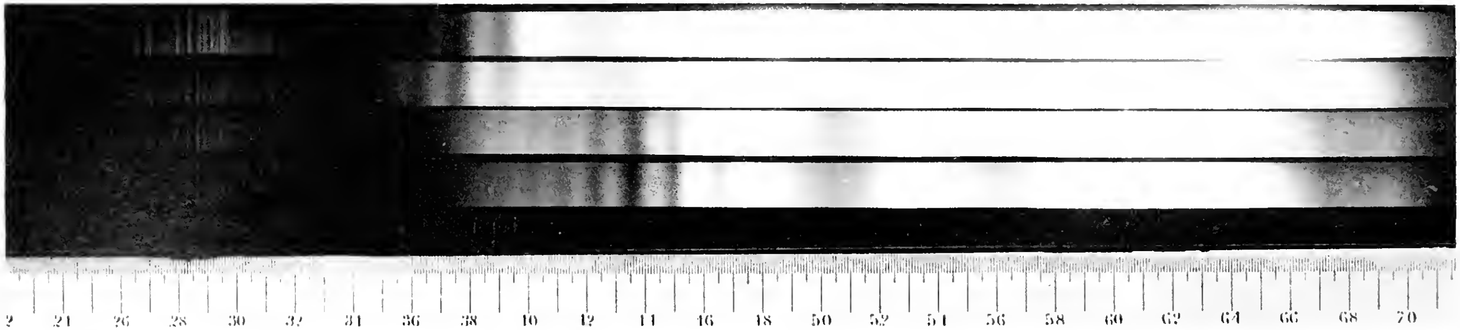


B

CAMPBELL ART CO., ELIZABETH, N. J.

CAMPBELL ART CO., ELIZABETH, N. J



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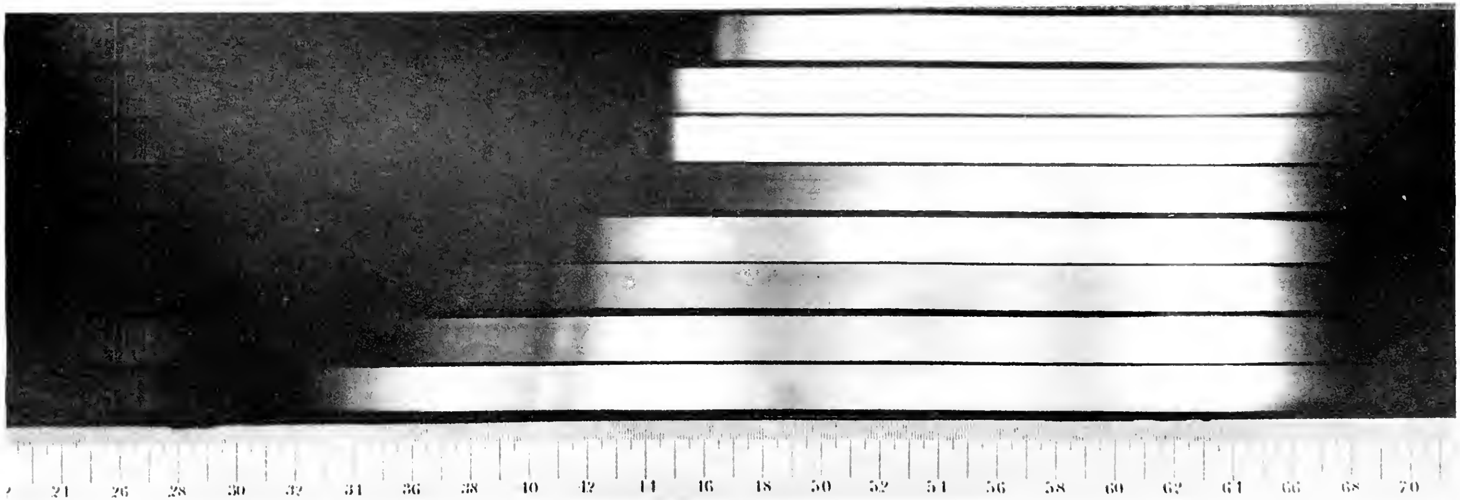

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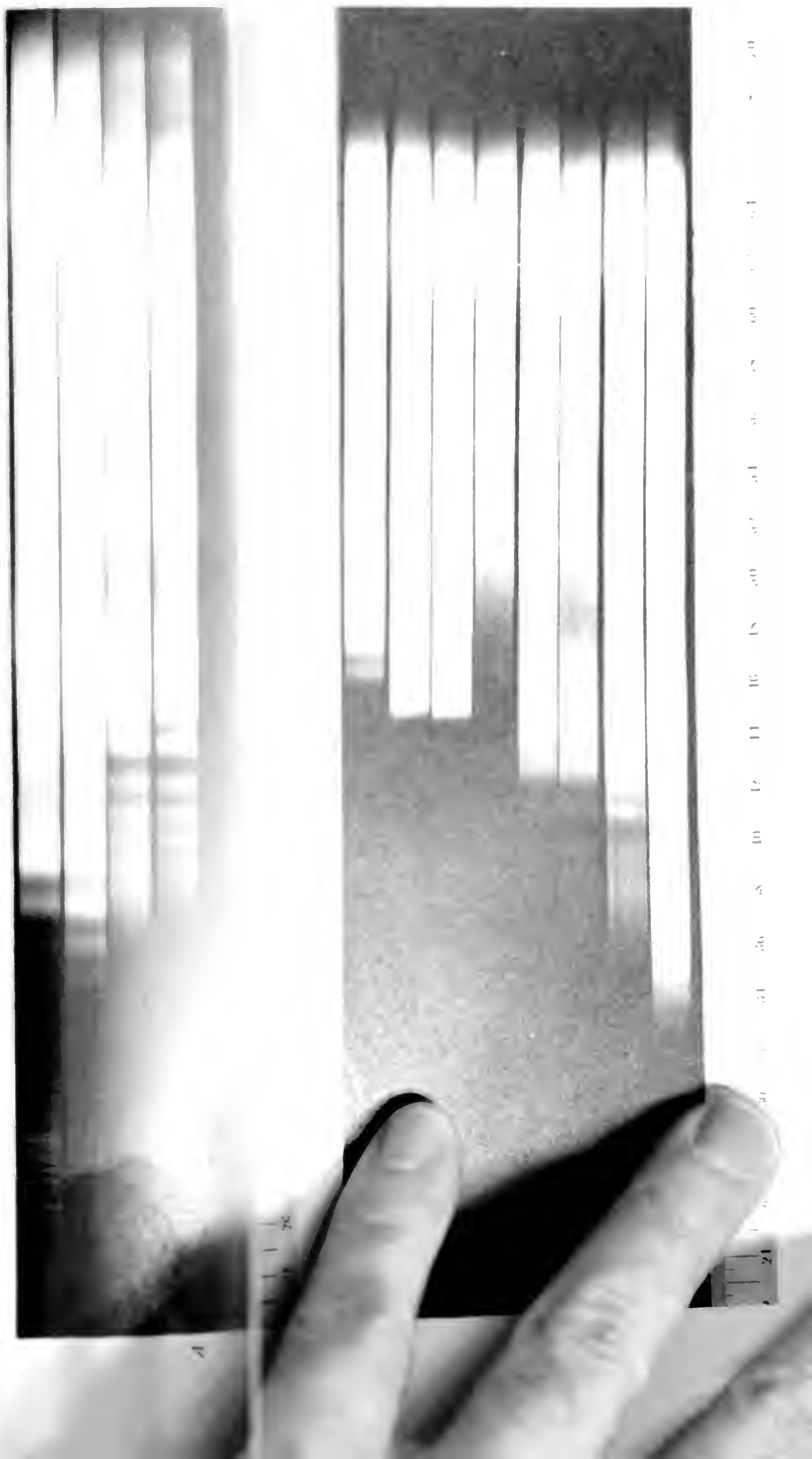

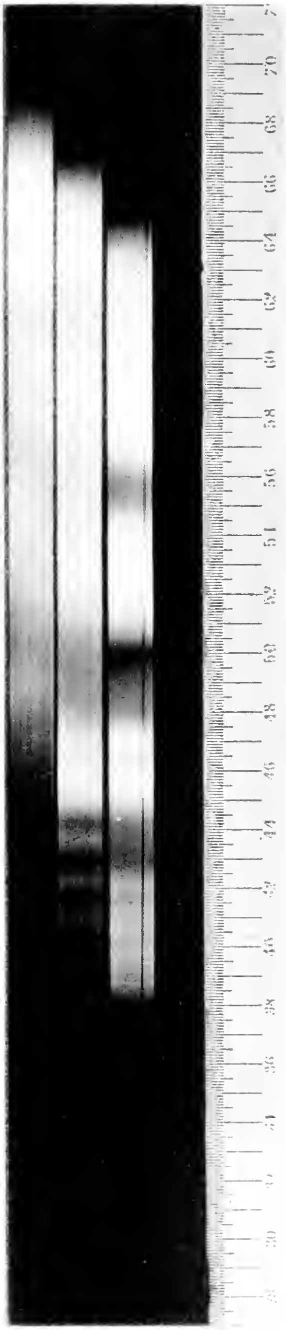

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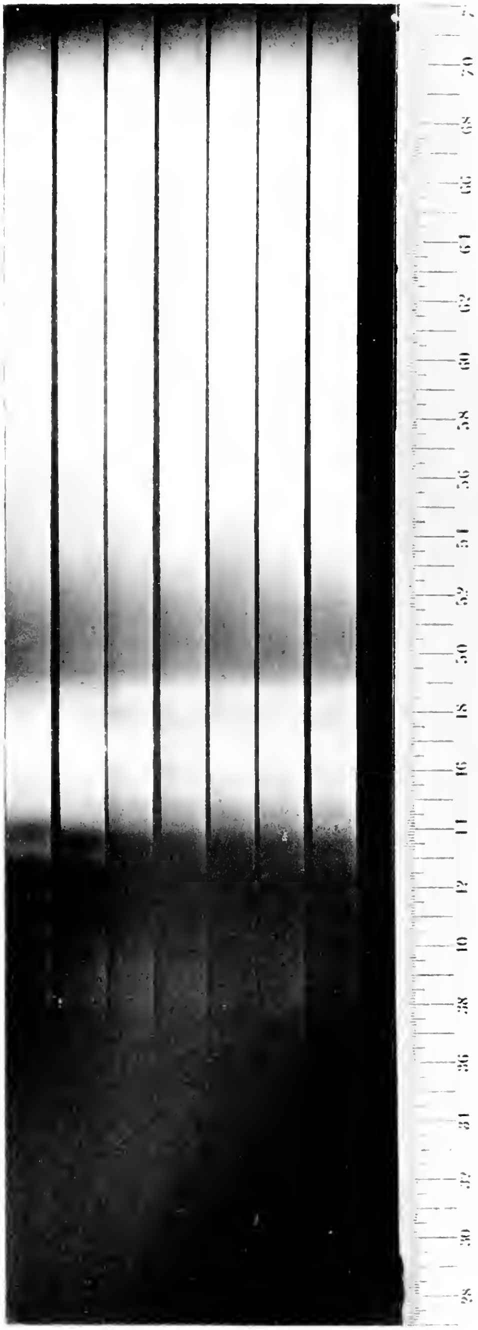

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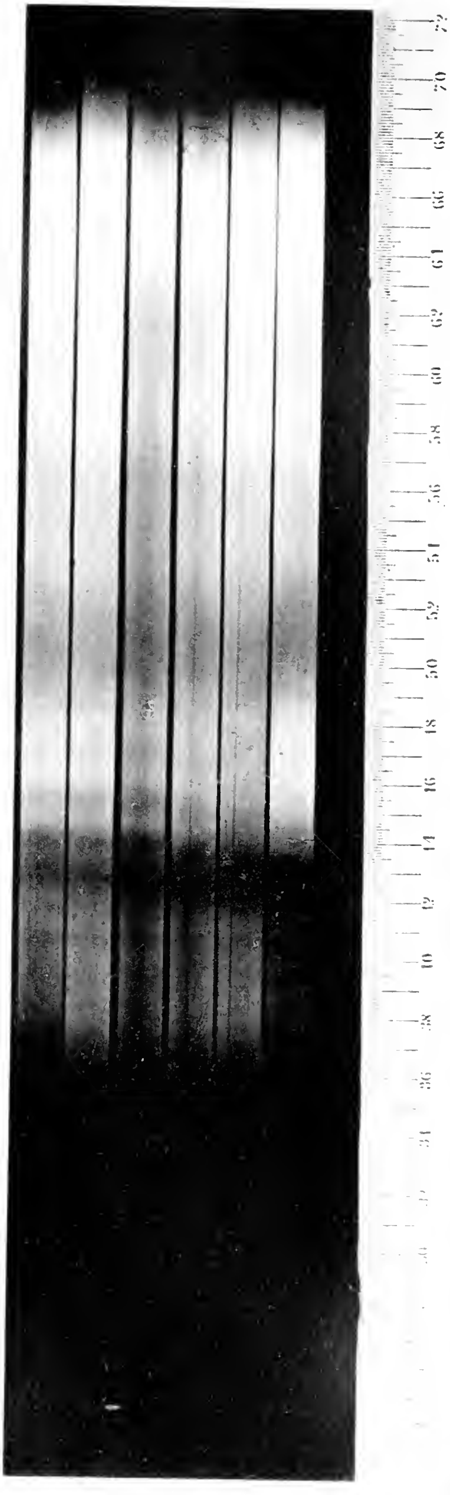
CAMPBELL ART CO., ELIZABETH, N



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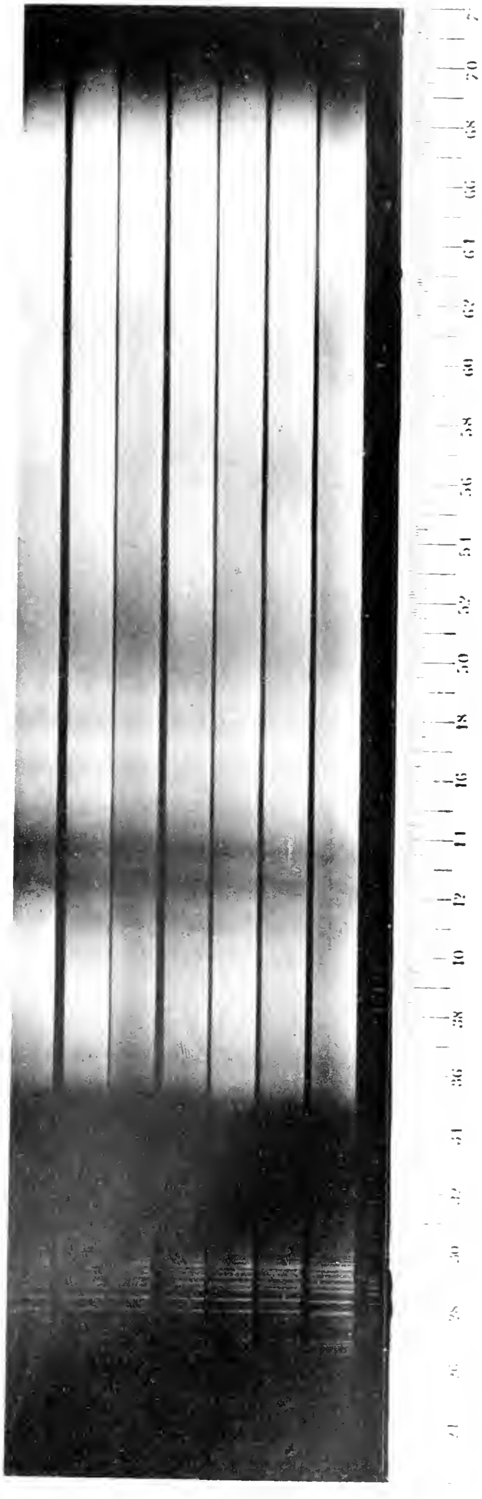

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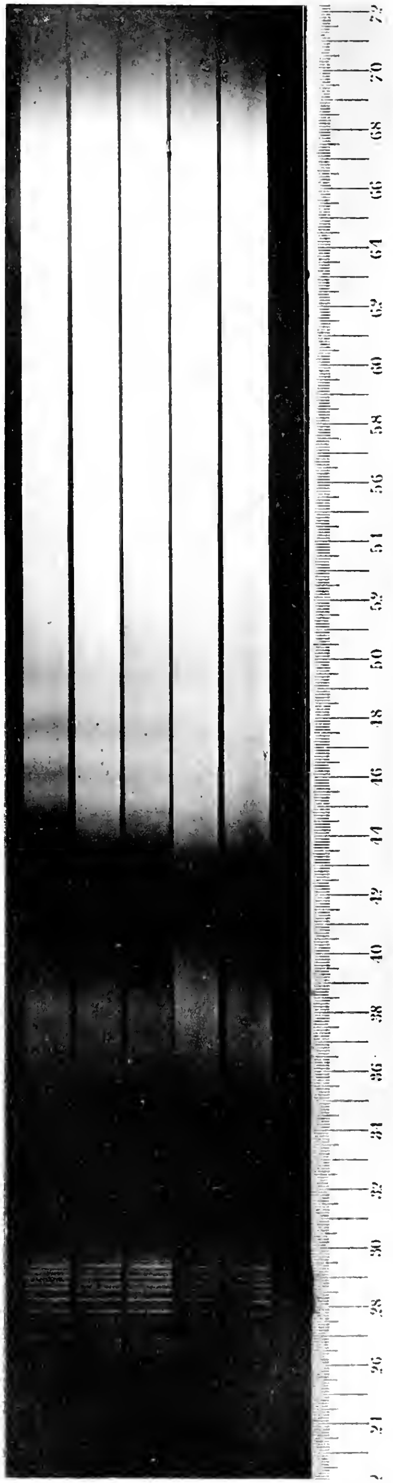
CAMPBELL ART CO., ELIZABETH, N. J.



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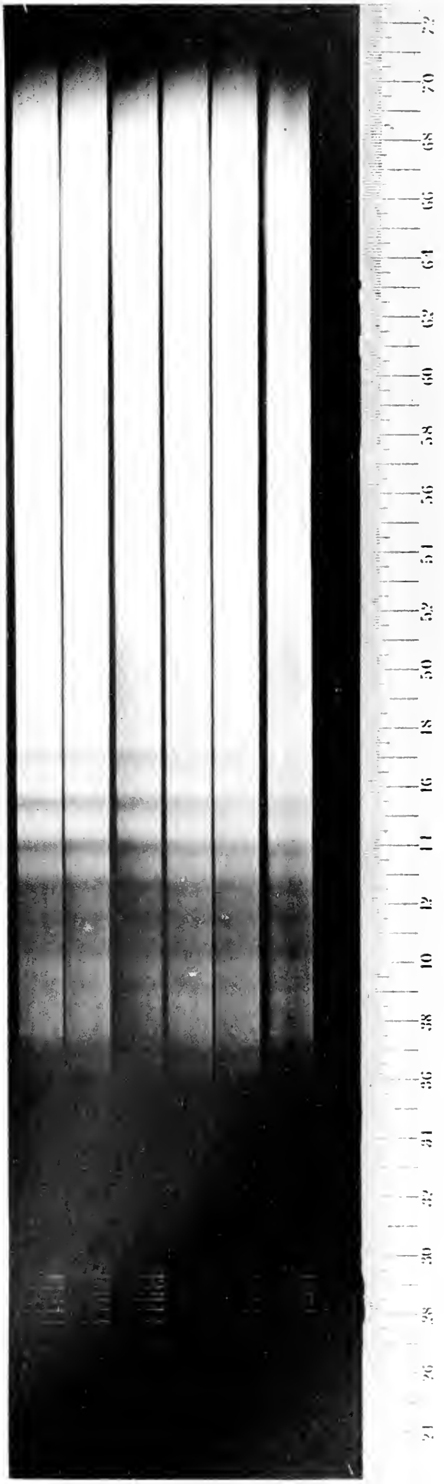

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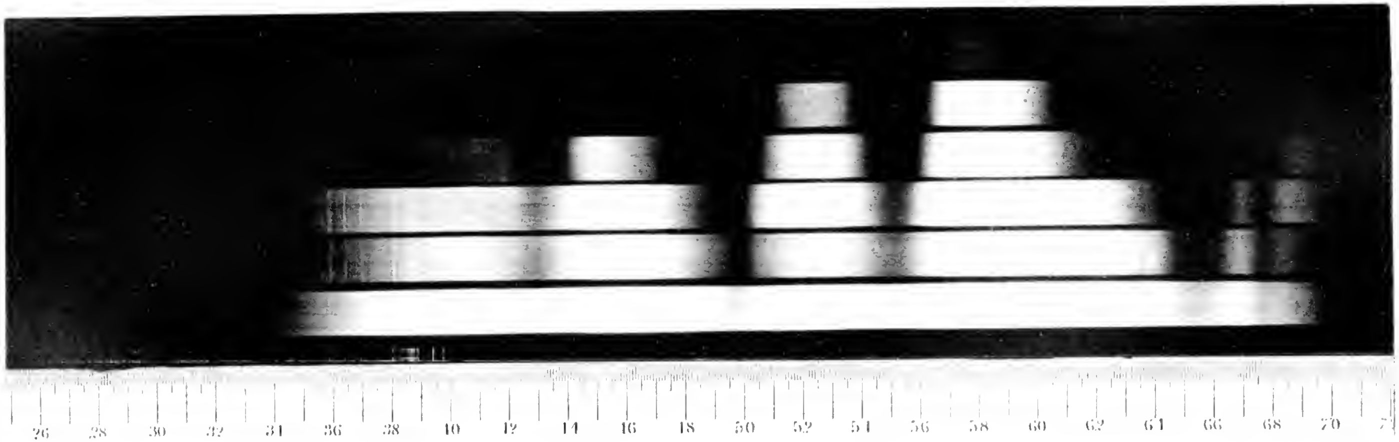

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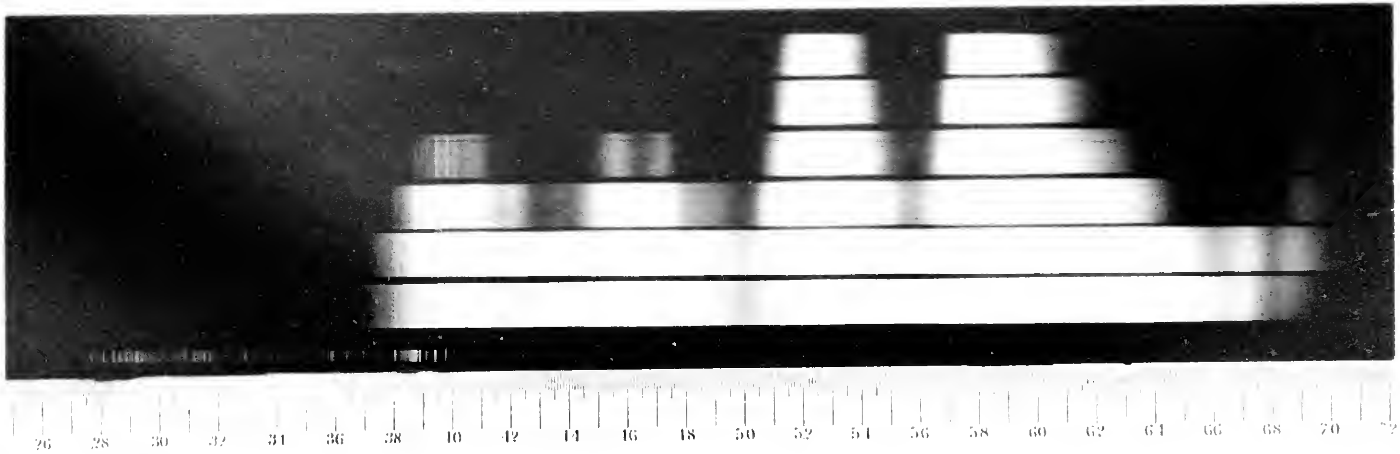

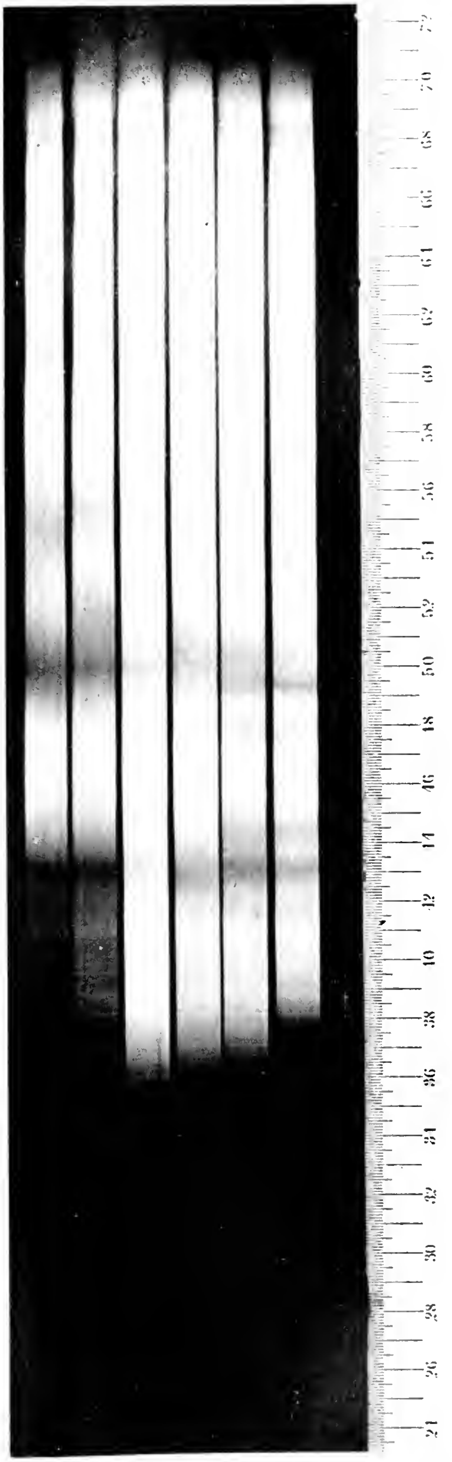

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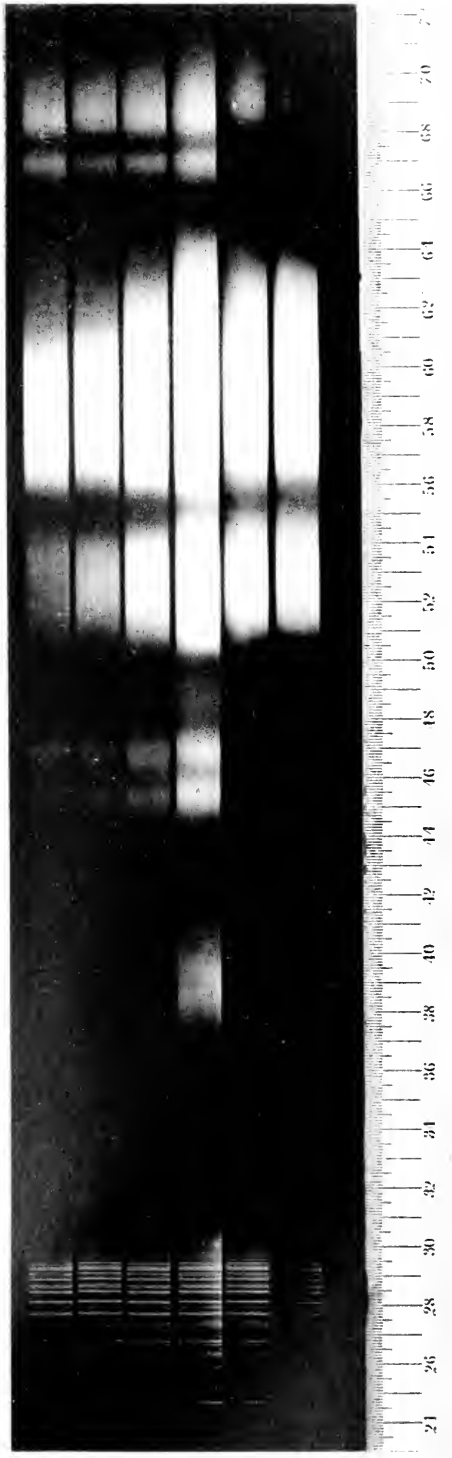

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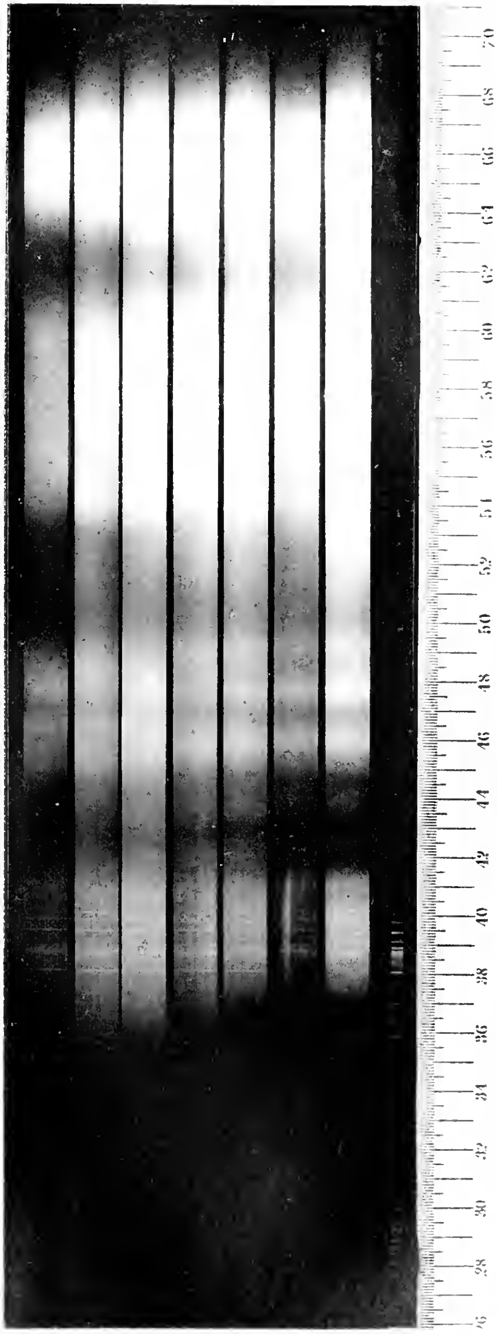

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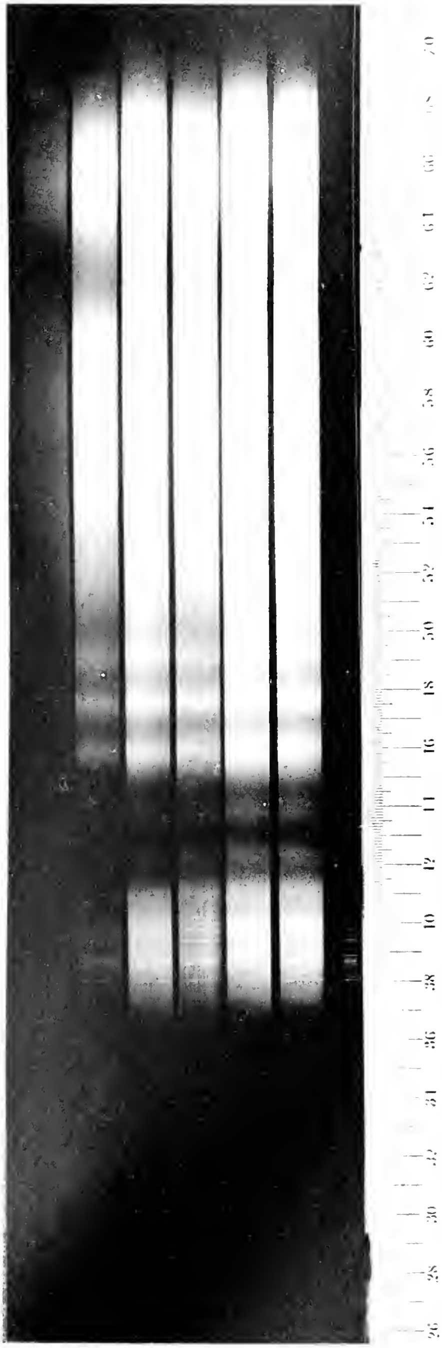

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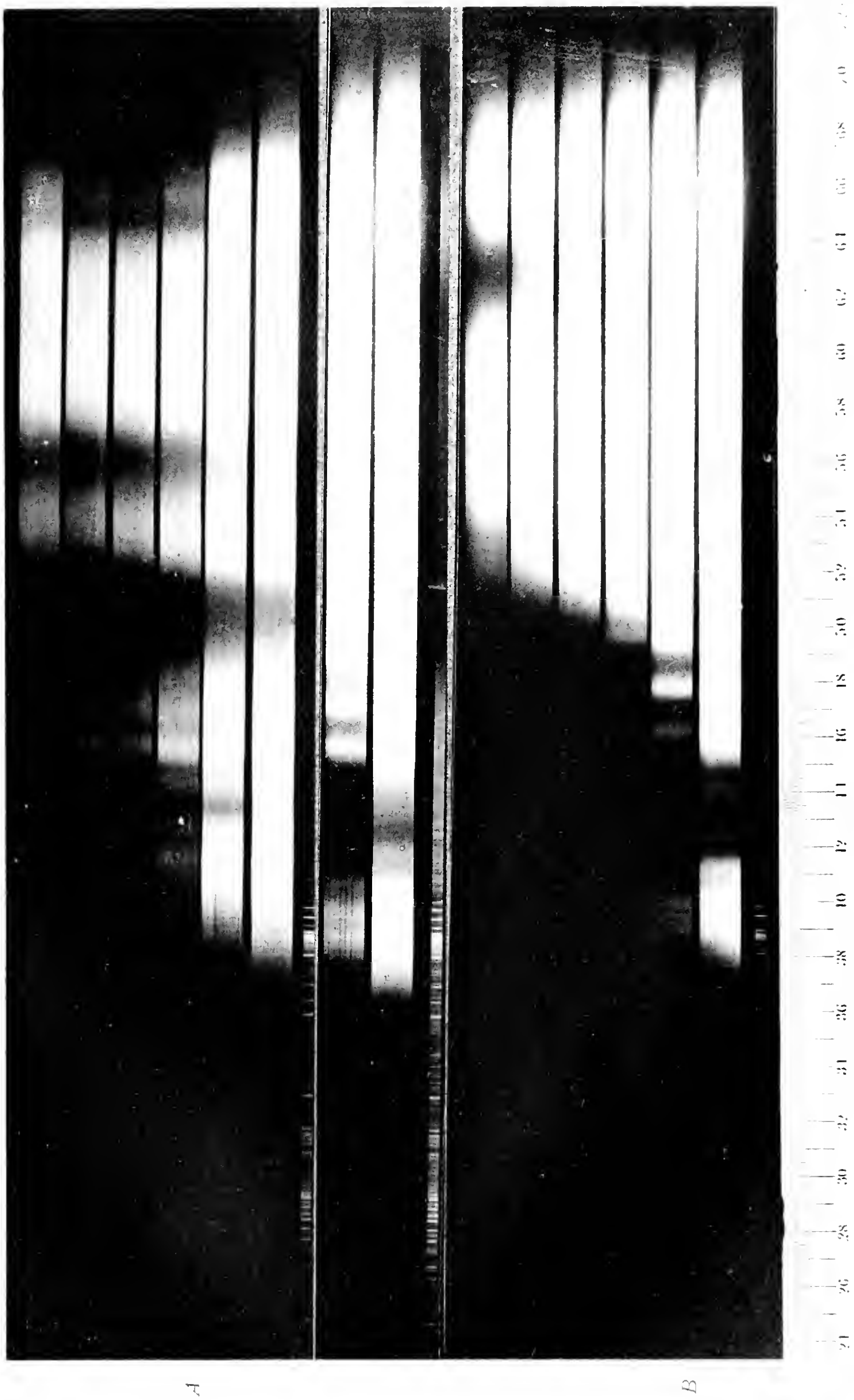

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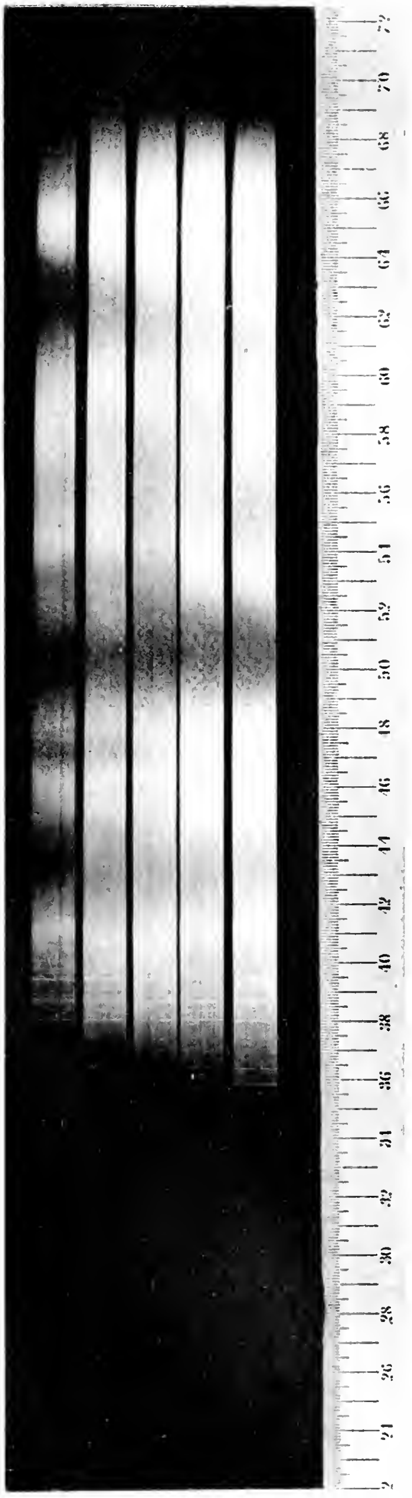

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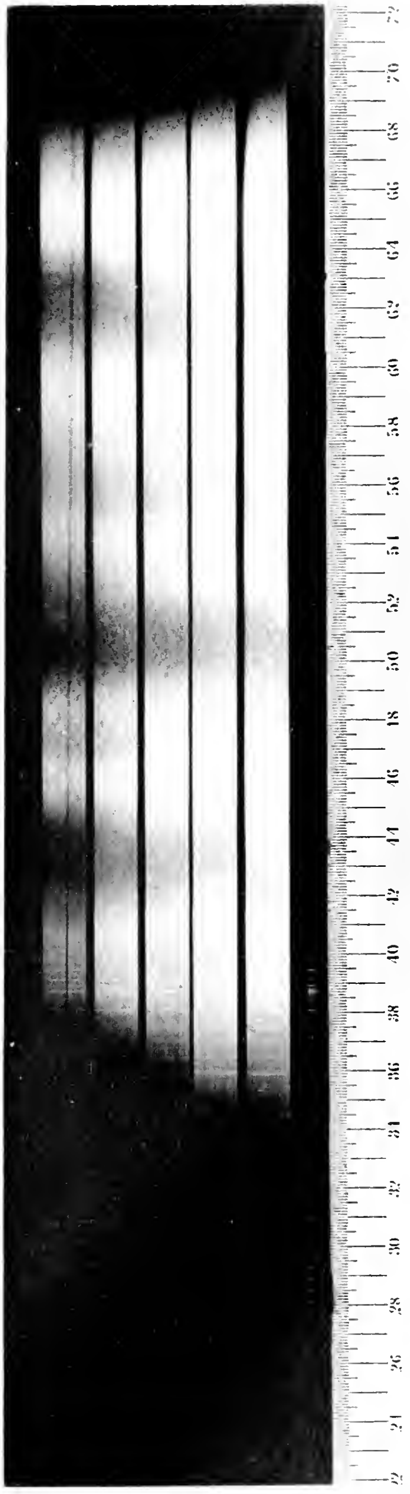

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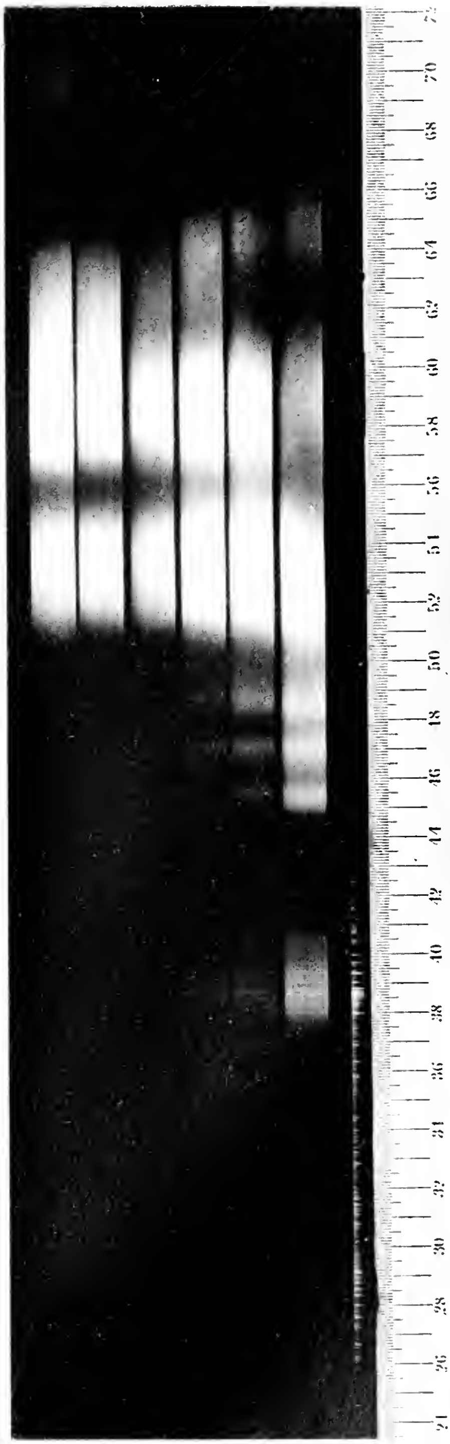
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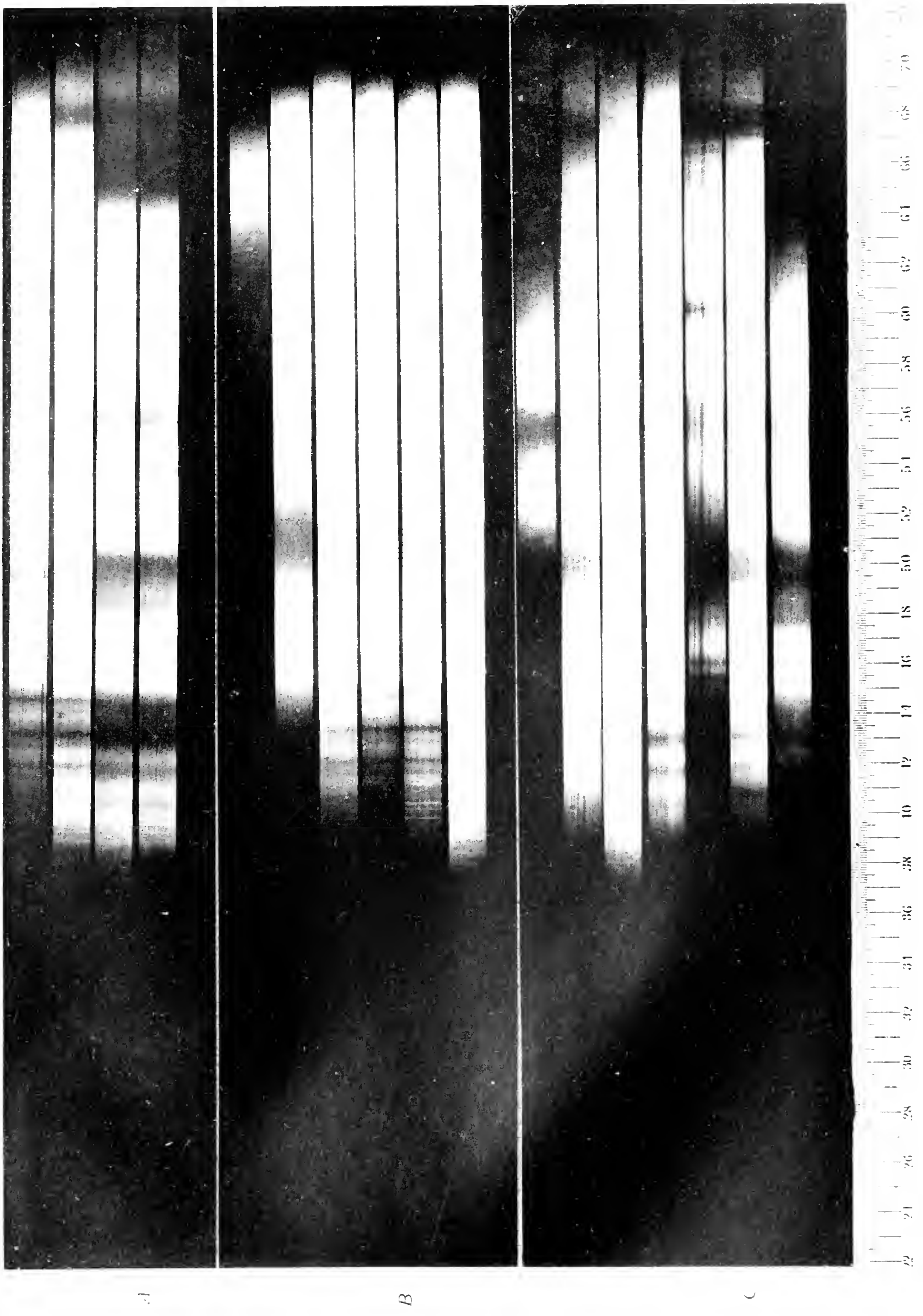
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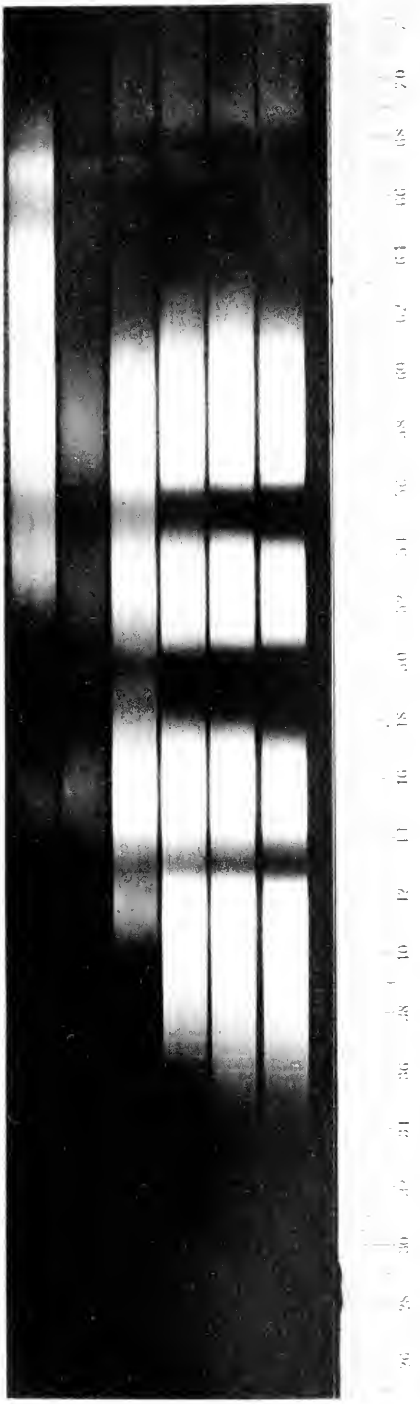

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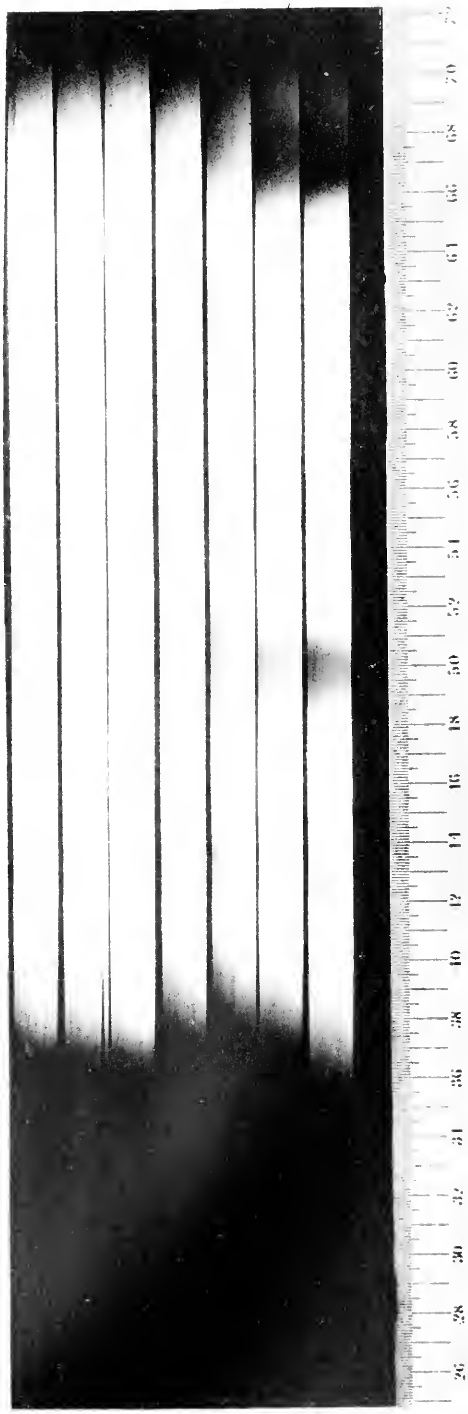

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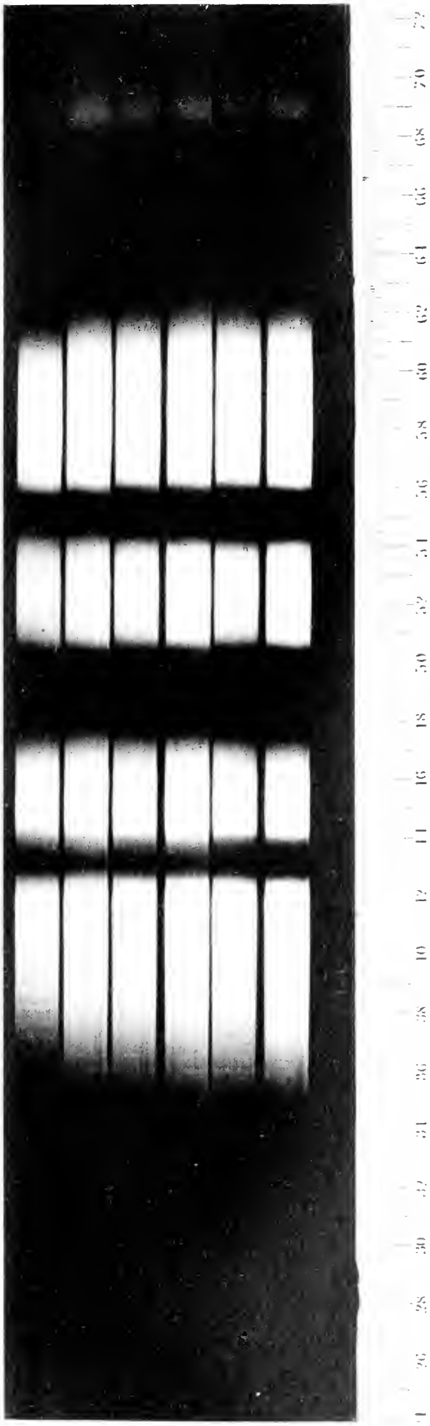
CAMPBELL ART CO., ELIZABETH, N. J.



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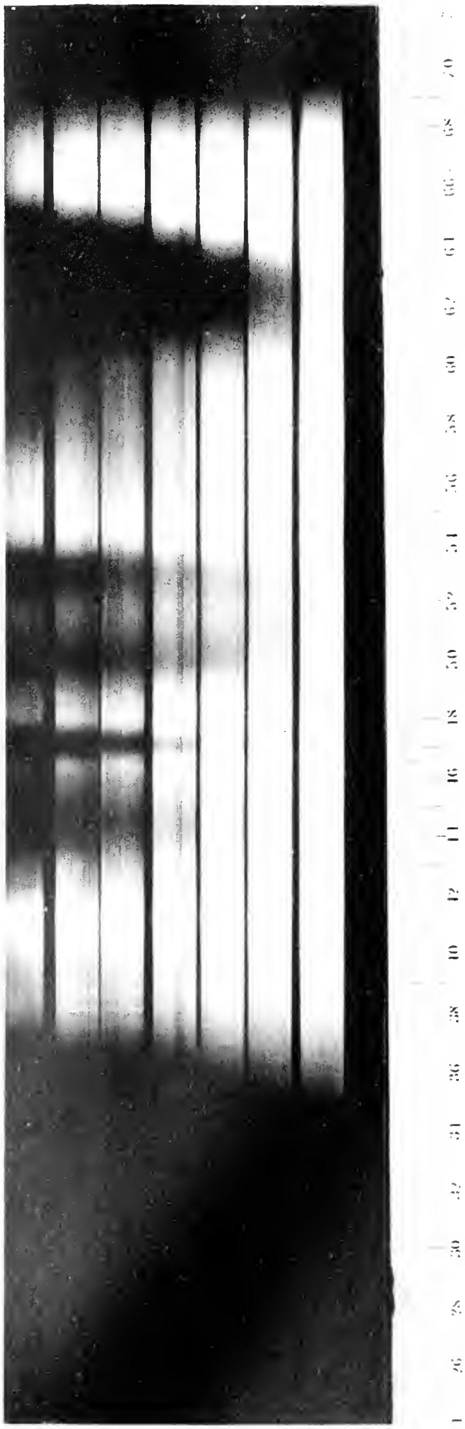

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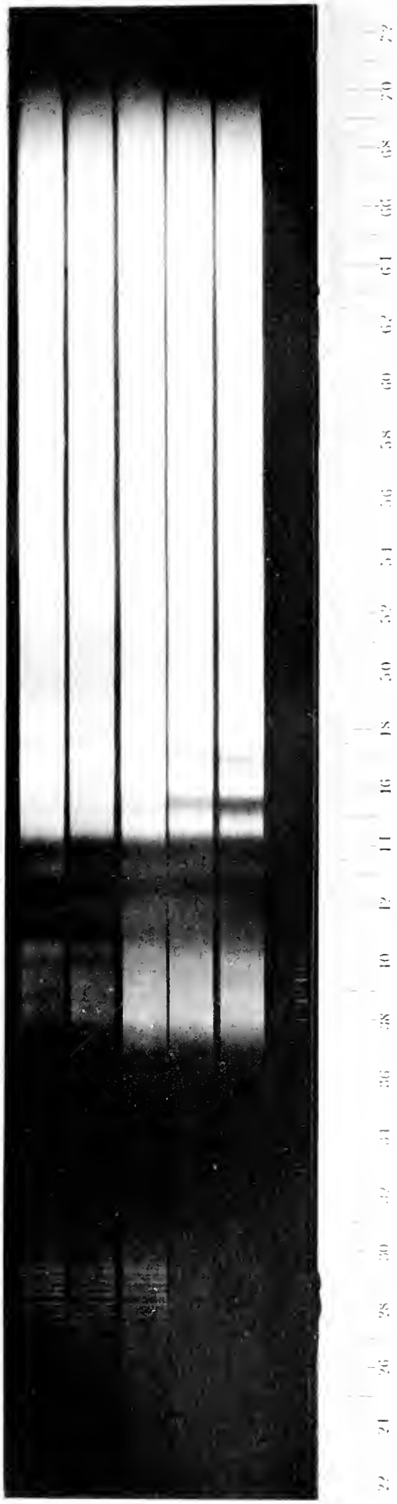
CAMPBELL ART CO., ELIZABETH, N. J.



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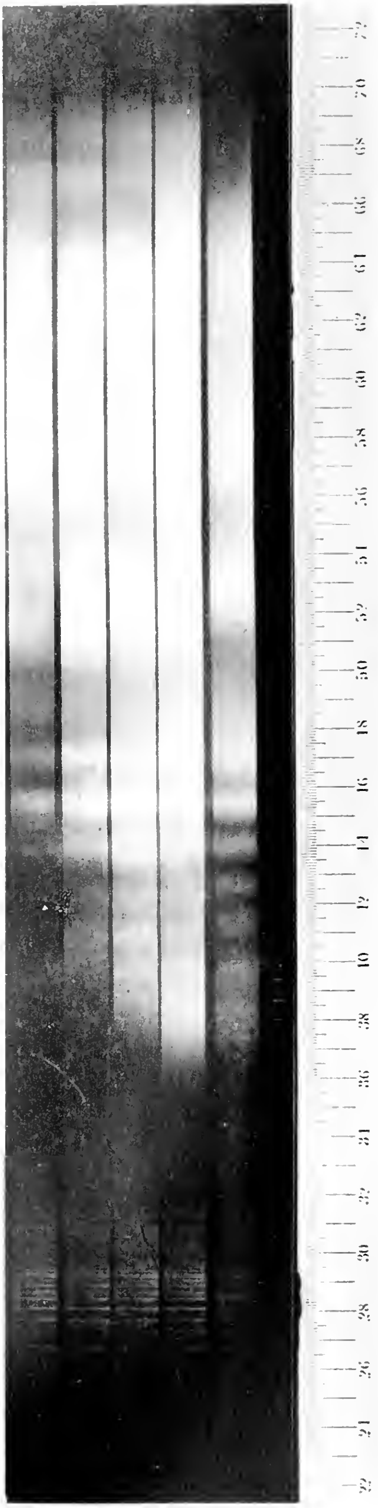

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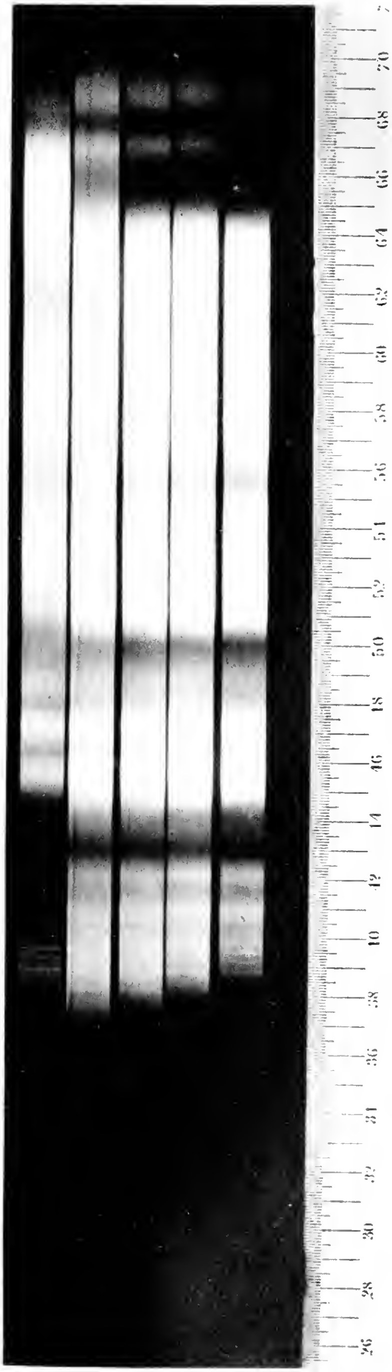
CAMPBELL ART CO., ELIZABETH, N. J.



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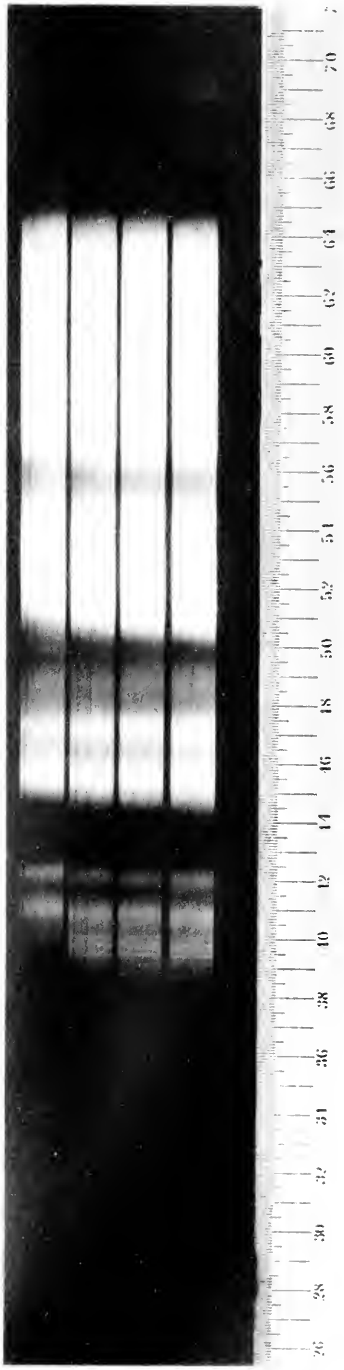

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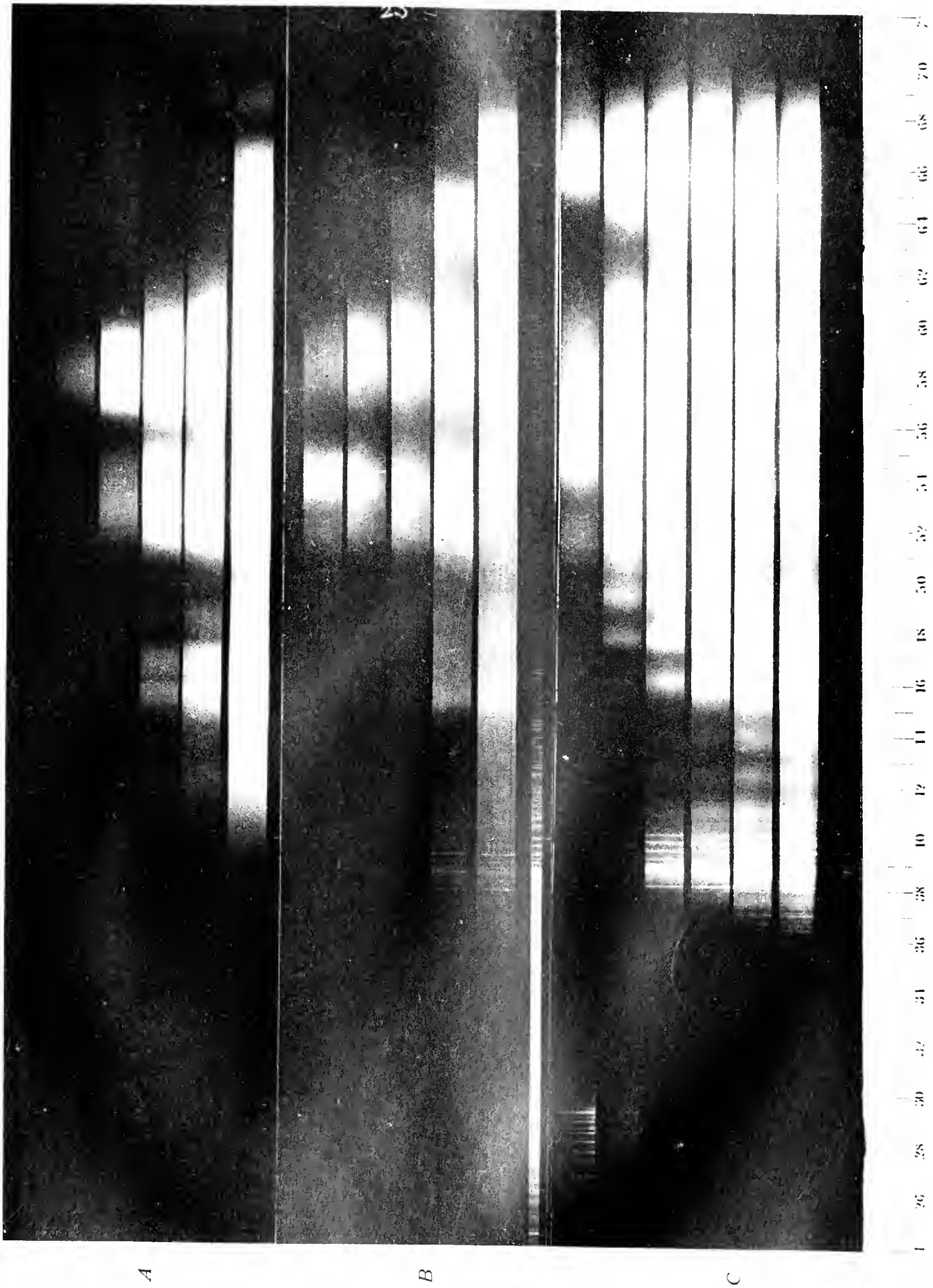
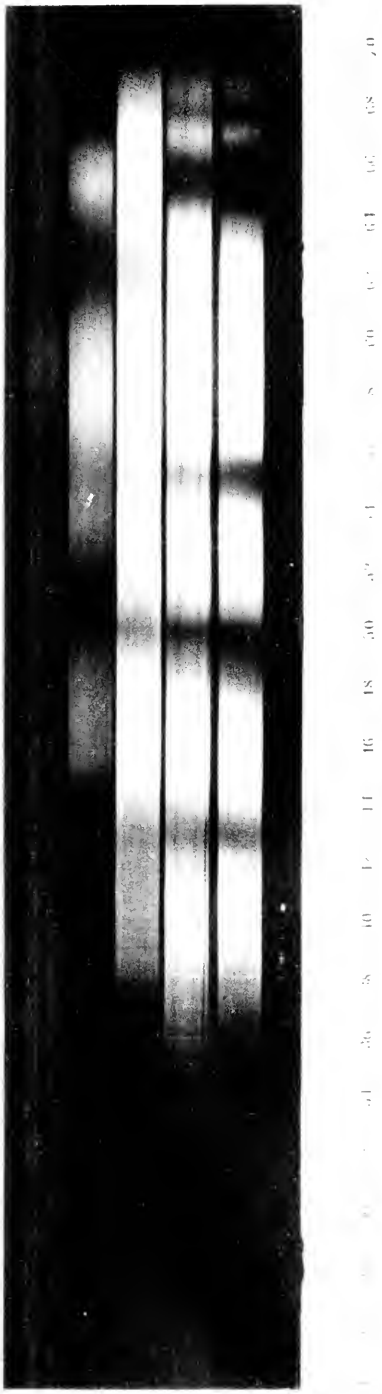
CAMPBELL ART CO., ELIZABETH, N. J.



AMPBELL ART CO. ELIZABETH, N

PLATE 96



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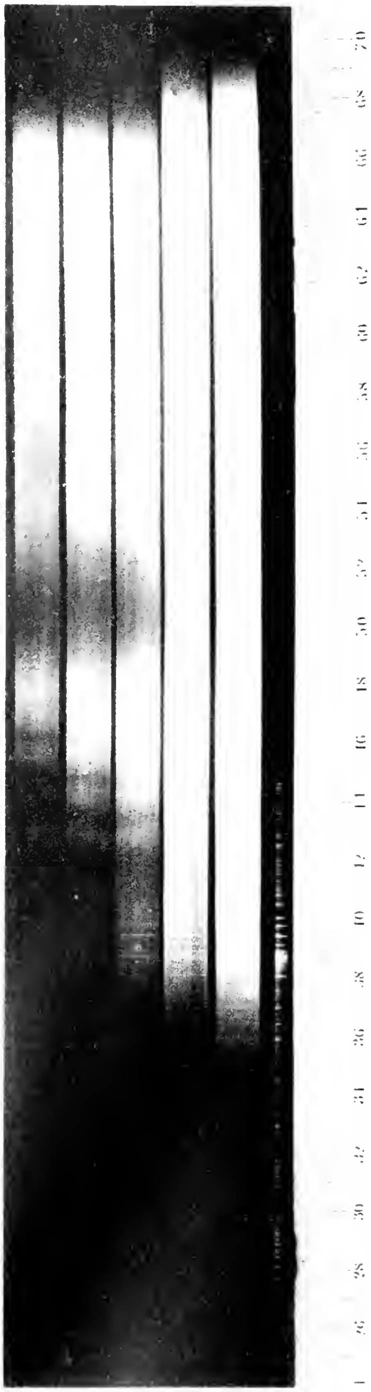

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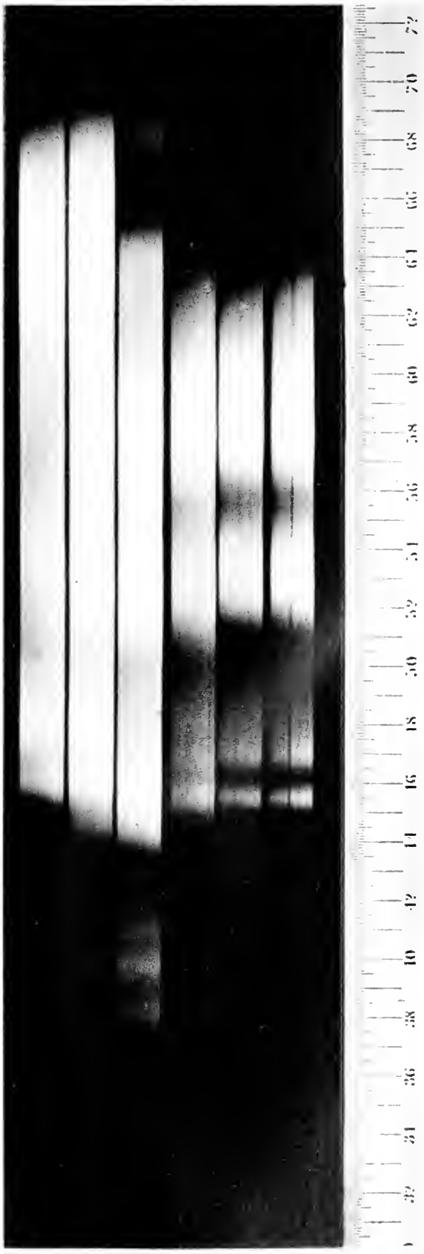
PLATE 97



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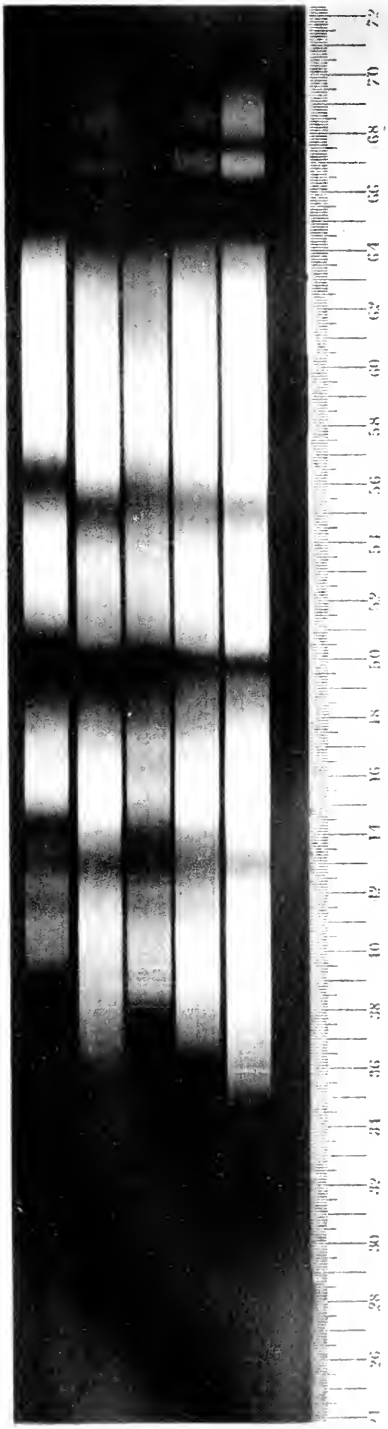
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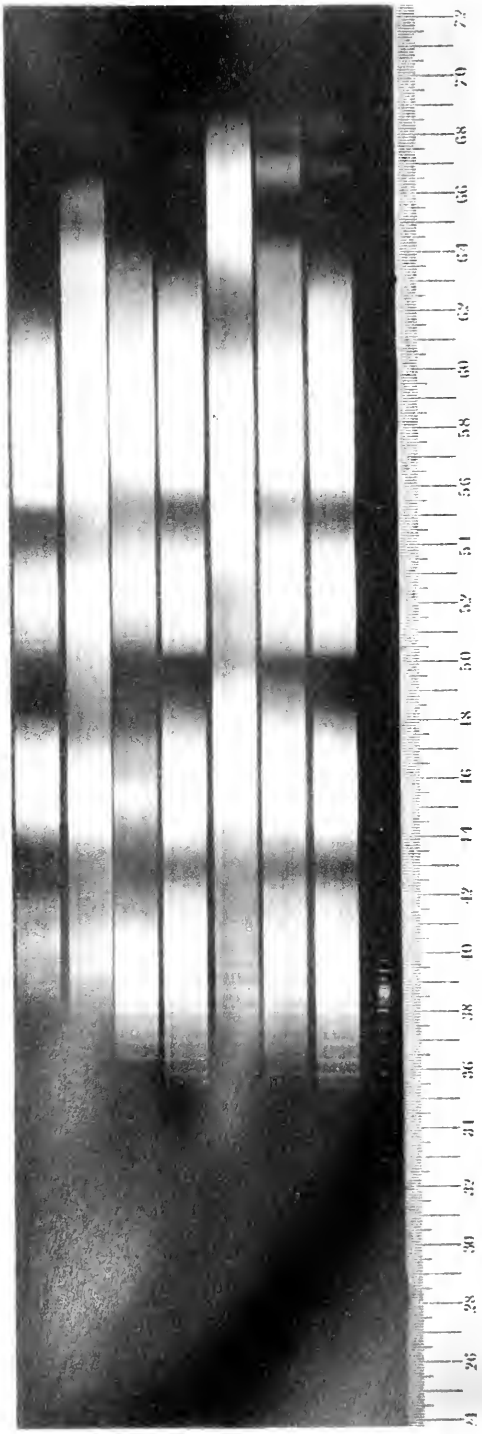
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