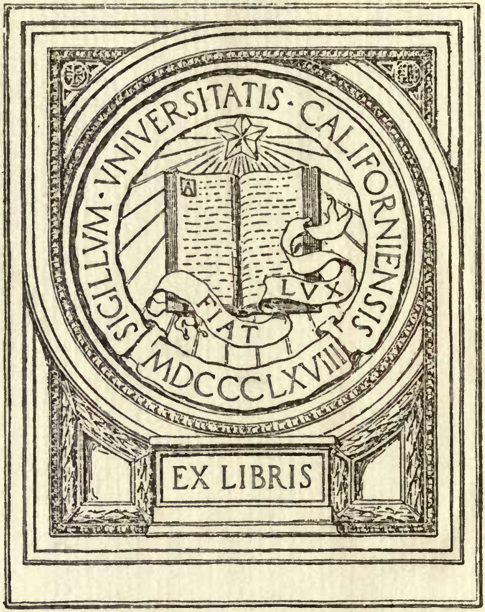

The Testing and Valuation of Raw Materials

USED IN

Paint and Colour Manufacture

· Testing Paint and Colour Materials ·

BY

M. W. JONES, F.C.S.

MEDAL AND HONOURS CITY AND GUILDS OF LONDON INSTITUTE
FORMERLY TEACHER AT THE ACCRINGTON TECHNICAL SCHOOL
AND THE WHALLEY (LANCS.) TECHNICAL CLASSES

LONDON
SCOTT, GREENWOOD & CO.
19 LUDGATE HILL
Publishers of the "Oil and Colourman's Journal"
1900

D. VAN NOSTRAND COMPANY,
NEW YORK.

ABERDEEN UNIVERSITY PRESS.

PREFACE.

This little text-book is intended merely to supplement the larger and more comprehensive works upon the subject. The demands made upon the laboratory of a large Colour Works are frequently heavy, and the operator is compelled to resort to analytical processes, which, whilst yielding results of fair comparative accuracy, do not take up the time occupied by others that carry the same to its extreme limits, and which may be more interesting from a purely scientific point of view.

The various processes given have been selected from numbers of others, after many years of experience, and it is hoped that the arrangement under separate headings, of the principal ingredients and impurities found in the various Raw Materials, will render this small work handy for reference, when it is desired to ascertain what is valuable or detrimental in the sample under examination.

M. W. J.

THE

TESTING AND VALUATION OF RAW MATERIALS

USED IN

PAINT AND COLOUR MANUFACTURE.

This important branch of work embraces the most tedious, but at the same time most valuable results which the chemist is called upon to produce; and as he has frequently to decide with rapidity and accuracy upon the respective merits of several samples tendered by competing firms, the following analytical processes are offered as a guide. By means of them the manipulator is enabled to produce the maximum of accuracy in minimum time, two essentials always to be considered in a busy laboratory, and which are not always attained by following the more classical processes given in some of the standard manuals.

Under the somewhat comprehensive heading of Raw Materials are placed the numerous articles which enter into the composition of paints and colours; but as the organic colouring matters form practically a class by themselves, and are usually tested comparatively, they will not be considered in this article; for although they can be fairly classified under the heading of Manufactured Chemicals, their numbers are so great that it is proposed to deal exclusively with inorganic colouring matters and chemicals. Consequently it will be set forth how the more important ingredients of these substances can be detected and estimated, and how the value of the sample under examination may be judged from the results so obtained.

It must of course follow that no unskilled observer can hope to produce reliable results even by close attention to the manipulations described. A certain familiarity with chemical analysis and methods is absolutely necessary, and these processes are offered in the hope that they will be found superior to many now in constant use.

ALUMINIUM COMPOUNDS.

Under this heading the most important substances that fall under our consideration are: aluminium sulphate or cake alum, the chemical composition of which is represented by the formula $Al_2(SO_4)_3 + 18\ H_2O$; the alums, which are double salts formed by combinations between aluminium sulphate and alkaline sulphates, and which are: aluminium potassium sulphate or potash alum, $Al_2(SO_4)_3 + K_2SO_4 + 24\ H_2O$; and aluminium ammonium sulphate or ammonia alum, $Al_2(SO_4)_3 + (NH_4)_2\ SO_4 + 24\ H_2O$. The value of these articles depends upon the amount of alumina (Al_2O_3) which they contain, and as a general rule a pure sample of aluminium sulphate is the most economical, as it should yield 15 per cent. of alumina, whereas potash alum yields only 10·8 per cent., and ammonia alum 11·9 per cent. But, on the other hand, the alums are generally preferred, as they come upon the market with a regular composition and of almost theoretical purity, and are consequently free from traces of iron salts and free acid, two defects from which aluminium sulphate has suffered in the past, but which have now been largely overcome by many manufacturers, although it is a rare occurrence to find a sample of cake alum which does not contain an appreciable quantity of iron salts. The chief inducement, however, for the use of aluminium sulphate instead of either of the alums, is the lower price at which it can be purchased, which usually shows an advantage to the user of from thirty-five to forty shillings per ton.

To estimate the amount of alumina in either of the substances enumerated above, it is necessary, first of all, to grind the sample to fine powder in a mortar, and then to weigh out accurately and carefully 10 grammes. This is placed in a beaker, which is then half-filled with distilled water, and perfect solution is obtained by heating the contents of the vessel over a Bunsen gas flame, stirring the liquid occasionally with a clean glass rod. In order to get rid of any insoluble matter, which if present would make the ultimate result too high, the contents of the beaker are next filtered through a Swedish filter-paper into a standard flask having a capacity of 1 litre (1000 cc.). The filter-paper is washed repeatedly with boiling distilled water until the liquid in the flask reaches almost up to the 1000 cc. mark. The flask is then set aside, and when its contents are thoroughly cold, it is shaken well, and made up carefully to the mark on the neck with cold distilled water. Shake up the contents of the flask once more, and for the purpose of the analysis take out from the made-up solution by means of a pipette, 200 cc., which in reality corresponds to 2 grammes of the original sample. This abstracted liquid is placed in a tall beaker, which is then half-filled with distilled water, and 20 cc. of a cold saturated solution of ammonium chloride (NH_4Cl) are added. Stir the whole with a glass rod, and add just sufficient ammonium hydrate (NH_4HO) to render the whole slightly alkaline. Heat the contents of the beaker up to the boil, stirring occasionally with the glass rod, then allow the flocculent precipitate which will have formed to settle. This precipitate is aluminium hydrate ($Al_2(OH)_6$), and it is next filtered on to a Swedish filter-paper which yields an ash of known weight on ignition. When all the precipitate is on the filter, it is well washed with hot distilled water, until the washings are free from ammonium hydrate, which is indicated by red litmus paper ceasing to turn blue.

The filter-paper with its precipitate is then placed to dry, either in the water-bath or in an air-bath heated to about 105° C., and when thoroughly dry the precipitate is separated as completely as possible from the paper, and the latter is ignited in a platinum crucible which has been previously tared. When the ignition of the paper is complete and only a white ash remains, the precipitate is carefully added, and the crucible and its contents are heated over the blowpipe flame for about two minutes. The crucible is then covered with a lid, placed under a dessicator to cool, and is then weighed.

To calculate the percentage of alumina from the results so obtained, it is necessary to deduct from the total weight of the crucible and its final contents, that of the crucible and filter-paper ash, which figures, multiplied by fifty, will give the percentage of Al_2O_3 in the original sample, and the result can be compared with the figures already given, which show the percentage of that substance in pure aluminium compounds.

The results of the analysis should always be set down in a book, so that future reference can be made at any time, and an excellent way of setting down the essential details in the above analysis is given below, and it will readily be seen that the same tabulated form will apply to the other raw materials yet to be considered, varying the statement of the substances found according to circumstances :—

Taken of sample of cake alum . . .	10	grammes.
Solution made up to	1000	cc.
Taken of made-up solution . . .	200	,,
Crucible + Al_2O_3 + Filter ash . . .	13·058	grammes.
,, + filter ash	12·762	,,
	= 14·8°/o Al_2O_3.	

The figures given are inserted only as a guide, but it is worthy of note that entries so made are invaluable for reference, and are accepted as evidence in legal cases.

Another very important test, and one that should never be omitted if the sample is intended for the production of Madder Reds, is that for iron, as the least trace of this impurity is very detrimental to the purity and brilliancy of the ultimate shade. Weigh out about 10 grammes of the sample, dissolve in a little distilled water, add two or three drops of pure nitric acid (HNO_3) and heat up to the boil. Allow the solution to cool, and divide it into two equal portions. To one add a few drops of a solution of potassium ferrocyanide (K_4FeCn_6), and to the other a few drops of potassium sulphocyanide solution ($KCNS$). A blue coloration or precipitate in the first solution, or a blood-red coloration in the second, indicates the presence of iron; whereas the absence of such results would show that the sample was free from the objectional feature. Should the presence of iron be indicated, the sample in question should be at once rejected, as it is quite possible to obtain aluminium products perfectly free from contamination with iron.

Although liquid aluminium products are not used to the same extent as the solid substances in the colour works, acetate of alumina of varying strength is occasionally met with, and in this case—as in the alums—freedom from iron, and the amount of available alumina present, forms the basis upon which the value of the sample is judged. The test for iron is performed exactly as described above; but as most samples of acetate of alumina contain varying amounts of undecomposed lead acetate, it is necessary to remove this before precipitating and estimating the alumina, the mode of procedure being as follows:—

Weigh out accurately in a small tared beaker 10 grammes of the sample, and make up to a litre in a flask with distilled water. From the made-up solution measure out by means of a pipette 200 cc., place this in a beaker which is then half-filled with distilled water. Add a few drops of pure hydrochloric acid (HCl), and pass a stream of sulphuretted hydrogen gas (H_2S) through for about ten minutes. Any precipitate thrown down in this operation is lead sulphide, and it must be carefully filtered off, the filter is then well washed and the whole of the filtrate well boiled in a flask until it ceases to smell of the H_2S gas, when it is poured into a beaker, ammonium chloride added, the whole rendered slightly alkaline with ammonium hydrate, and the remainder of the operation is conducted exactly as described for the estimation of alumina in the solid aluminium compounds.

CHINA CLAY.

This useful white pigment, which enters largely into the composition of paints and colour bases, is considered here for the sake of convenience; although the analysis of an average sample will show that this substance contains rather more silica (SiO_2) than alumina. It may be looked upon as a compound of silica and alumina, and a pure sample should correspond to the lengthy formula $2\ SiO_2 + Al_2O_3 + 2\ H_2O$, in which the percentage of the various ingredients would be represented somewhat as follows: SiO_2 47: Al_2O_3 40: Water 13.

Samples should be tested comparatively for purity of shade, freedom from grit, and covering power, and a knowledge of the ultimate use of the sample will guide the operator in judging the results; although, as a general rule, a sample intended for use in paint mixtures need not possess such a pure white shade as one required for a lake base, and in the latter connection it is useful to know that china clay possesses greater letting down, or colour absorbing capacity, than an equal weight of barytes.

Owing to its cheapness, china clay is never adulterated, and consequently no complete analysis is ever required in the colour works laboratory, although if such was desired in extreme cases, the following method may be followed:—

Weigh 5 grammes of the sample into a tared platinum crucible and heat over a Bunsen gas flame for about an hour, finishing up with a vigorous heating for about five minutes over the blowpipe flame. The crucible with its contents is then cooled under a dessicator and weighed, the loss in weight calculated to percentage, indicating the amount of combined water present, which should not greatly exceed the figures given above.

To decompose the sample for the purpose of separating and estimating its two principal ingredients is the next operation, and this is performed by fusing the residue from the last process, with about 15 grammes of a mixture of sodium and potassium carbonates in about equal proportions. This is performed by heating over the blowpipe flame until the whole fuses into a clear glass-like liquid, but should any white portions of undecomposed china clay be observed after prolonged heating, more of the mixture of carbonates must be added, until the fusion is complete. When this is accomplished, the crucible is set aside to cool, and afterwards placed in a large beaker, which is covered with a clock-glass. Pure dilute hydrochloric acid in excess is now added to the beaker, and when the effervescence ceases, the crucible and the under side of the clock-glass are rinsed with distilled water into the beaker, the contents of which are then transferred to a porcelain basin, and evaporated to complete dryness. The residue is then heated with pure hydrochloric acid, and the whole is filtered through a Swedish filter-paper, the filter being well washed with boiling distilled water until free from acid, which is indicated by blue litmus paper ceasing to turn red. The filtrate and washings now contain the whole of the alumina, which can be estimated as already described, but as the precipitate obtained from so large a quantity of the original sample would be somewhat bulky, it would be better to make the filtrate and washings up to 500 cc. in a standard flask, and use 100 or 150 cc. of the made-up solution for the estimation of alumina. The residue upon the filter is silica, and this is estimated by drying the paper and its contents in the air-bath, afterwards igniting the same in the manner already described, in a tared platinum crucible, the increase in weight between the two weighings indicating the amount of silica (SiO_2) contained in 5 grammes of the sample under examination. The results so obtained should vary but slightly from the percentage composition given.

IRON COMPOUNDS.

Under this heading we find two distinct classes of salts in use, *viz.:* ferrous and ferric; but owing to the readiness with which the former becomes oxidised into the latter, we but rarely come across a perfectly pure ferrous salt, at least in the works.

Under the first of these classes, the most important substance is ferrous sulphate crystals, also known as green vitriol and copperas, which possesses a chemical composition represented by the formula $FeSO_4 + 7\ H_2O$. Under the same heading we have also ferrous acetate, or pyrolignite of iron, $Fe(C_2H_3O_2)_2$, a compound better known under the name of "Black Liquor".

Under the classification of ferric compounds we find that the two most important substances in general use are ferric chloride, Fe_2Cl_6, and ferric nitrate, $Fe_2(NO_3)_6 + 18\ H_2O$.

The various oxides of iron which enter so largely into the manufacture of paints form of necessity a class by themselves, but by far the most important of these is ferric oxide Fe_2O_3, which forms the bulk of the number of pigments which are sold under such names as light and dark red, red oxide, Venetian red, Indian red, purple oxide, etc. In the form of hydrated oxide the same substance is known as York Brown, and it also forms the bulk of the well-known umbers, ochres, and siennas of commerce.

The analysis of these iron compounds is by no means complicated, and is generally confined to an estimation of the amount of iron oxide present. In the case of ferrous sulphate crystals this is readily performed by titrating with a standard solution of permanganate of potash ($KMnO_4$), in what is known as the volumetric method. If it is desired to estimate the amount of iron present (both ferrous and ferric) in the sample, the method given under the analysis of ferric compounds must be followed, but where the amount of available ferrous salt only is required, the following method can be performed, and it yields accurate and rapid results.

Weigh out carefully 5 grammes of the powdered crystals, dissolve in cold distilled water with frequent stirring, and make up to 500 cc. in a standard flask. From this made-up solution measure out 50 cc. by means of a pipette, and place in a clean flask or white porcelain basin. Add about 250 cc. of distilled water, and 0·5 cc. of pure sulphuric acid (H_2SO_4) and titrate with a standard solution of potassium permanganate, taking care to stir or shake the liquid in the flask or basin whilst the standard solution is dropping in. If working with a flask it will be necessary to place a white porcelain plate underneath, in order to see the slight change of colour which indicates the end of the reaction. The standard solution is carefully dropped in, until after stirring the whole retains a very faint pink tint, at which point the reaction is said to be complete. In other words, all the ferrous salt has been converted into the ferric condition by oxygen absorbed from the permanganate of potash. The number of cc. of the standard solution required to produce this result is then read off from the burette, and, if multiplied by 200, will give the number of cc. required by 100 grammes of the original substance, and as every 100 cc. of the standard solution should equal 0·56 gramme of iron (Fe) or 0·72 gramme of FeO, or 2·78 gramme of $FeSO_4 + 7H_2O$, it is a simple matter to calculate the percentage of ferrous salt present in the original sample. As a guide it may be stated that the amount of such iron present in a perfectly pure sample of ferrous sulphate crystals is 20·14 per cent., but such purity is never met with in commercial samples.

The standard solution alluded to above is made by dissolving 3·156 grammes of pure dry potassium permanganate in 1000 cc. of distilled water, but as such solutions vary slightly in strength, especially upon keeping, it is best to check the strength before use, by titrating previously upon a definite amount of the easily procurable pure salt ferrous ammonium sulphate ($Fe(NH_4)_2 (SO_4)_2 + 6 H_2O$), in the manner described below. This salt always contains a definite proportion of iron—exactly one-seventh of its weight—and if we weigh out exactly 0·7 gramme (equal to 0·1 gramme of iron) and dissolve the same in about 150 cc. of distilled water in a white porcelain basin, then add one or two cc. of pure sulphuric acid, and drop in slowly from a burette the standard solution, stirring constantly until the liquid in the basin retains a faint pink colour, we shall find if the permanganate solution is of the proper strength that 17·85 cc. are required. Having thus found the strength of the standard solution in the equivalent of iron, it is an easy matter to work out the results obtained in the analysis of the sample under examination.

Owing to the presence of organic matter in ferrous acetate, or black liquor, we cannot estimate the amount of ferrous salt contained therein by the above method, as the permanganate solution would be acted upon by the organic matter present, and the results would be too high. Neither can we use that method for the estimation of ferric salts, therefore the following gravimetric method is applicable to both ferrous acetate and ferric solutions generally.

Weigh out carefully in a small beaker 20 grammes of the liquid and make up to 500 cc. in a standard flask with distilled water. From this made-up solution take out by means of a pipette 100 cc. and place in a medium-sized beaker, which is then half-filled with distilled water, add three or four drops of pure nitric acid (HNO_3) and heat the contents of the beaker up to the boil. Set the beaker aside to cool, then render the liquid slightly alkaline with ammonium hydrate, heat again up to the boil with constant stirring, and then set aside and allow the precipitate to settle, filter it off on to a Swedish filter-paper, wash the precipitate upon the filter paper with boiling distilled water until the filtrate is free from ammonium hydrate, then dry the filter-paper and precipitate in an air-bath heated to about 105° C., and when thoroughly dry, separate as completely as possible the precipitate from the paper, and ignite the latter in a tared platinum or porcelain crucible, and when the ignition is complete and nothing remains but a white ash, add the rest of the precipitate, and then heat the crucible and its contents over the blowpipe flame for three or four minutes. When cooled under a dessicator, the whole is weighed, and from the total weight that of the crucible + filter-paper ash is subtracted, and the result gives the amount of ferric oxide (Fe_2O_3) contained in 4 grammes of the original liquid, and by multiplying the result so obtained by 25, and calculating from the fact that every 160 parts of Fe_2O_3 contain 112 parts of iron (Fe), the expression of the result in the desired terms is easy.

Owing to the varying composition of the various oxides of iron—which, as we have seen, enter so largely into the composition of paints—they are rarely pure, and frequently contain large amounts of sulphate of lime (gypsum), silica (sand), alumina, and other impurities. The value of all is however judged by the percentage of iron which they contain, and the following process for its estimation can be followed :—

Weigh out 5 grammes of the sample, and place in a small beaker, and dissolve with a mixture of nitric and hydrochloric acids in about equal proportions. This is effected by boiling the contents of the beaker until the original colour of the sample has entirely disappeared. When this is accomplished, the contents of the beaker are carefully washed with distilled water into a porcelain basin, and the solution is evaporated to complete dryness, with frequent stirring. After the residue has cooled, it is warmed with a little dilute hydrochloric acid, and the solution is filtered through filter-paper, which is well washed with boiling distilled water, until the solution and washings nearly reach to the mark on the neck of a standard 500 cc. flask, into which they must be allowed to run. Should any residue remain on the filter, it will consist of barytes or silica, and the amount can be estimated, by drying and afterwards igniting in a platinum crucible. The solution in the standard flask is then set aside to cool, and when quite cold, distilled water is added up to the mark, and the whole well shaken to ensure perfect mixing. The iron present in this solution can be estimated by the gravimetric or precipitation method, already given for the analysis of ferrous acetate and ferric salt solutions; but if any alumina was present in the original sample, it would be precipitated along with the iron, and the result would be too high. It is therefore better to avoid this, and to estimate the iron by means of the standard solution of permanganate of potash already alluded to. Owing to the presence of nitric acid in the solution this cannot be done directly, and therefore we measure from the made-up solution, 250 cc. which is equal to 2·5 grammes of the sample, place the liquid in a beaker, precipitate the iron present by dilute ammonium hydrate, and wash the precipitate several times by decantation with hot distilled water. The washed precipitate is then dissolved by warming with dilute pure sulphuric acid, the liquid is carefully transferred to a small flask, and the iron is reduced completely by hydrogen liberated from pure granulated zinc, which is acted upon by the acid present. This is best performed by fitting into the neck of the flask, what is known as a Bunsen's valve, which simply consists of an india-rubber cork through which a piece of bent glass tube projects. The outside end of the tube is covered with a piece of tight-fitting rubber tube, which has a slit in it just below where the glass tube ends, and the extreme end of the rubber tube is closed by a short glass rod. This arrangement permits the steam and hydrogen gas to escape, but does not allow air to enter the flask, the contents of which become perfectly reduced. The action of the acid upon the zinc is accelerated by warming the contents of the flask, and when the gas ceases to bubble off, the liquid is ready for the titration. This process is performed exactly as previously described, but it will be necessary to place a white plate under the flask in order to see the end of the reaction. In calculating the results, the same factors are employed as in the previous description.

If it is desired to estimate the amount of alumina and calcium salts present in the original sample, we proceed as follows. From the made-up solution already described take out 200 cc., add a few drops of ammonium chloride, and render alkaline with ammonium hydrate. The liquid, which should be in a beaker, is then raised to the boil with frequent stirring, and is then set aside to cool, during which the precipitate settles. This is then filtered off through a Swedish filter-paper, and the precipitate on the filter is well washed with boiling distilled water, the whole of the filtrate being carefully kept for a subsequent operation. The filter-paper and precipitate are then dried and ignited, and after deducting the weight of the crucible and filter-paper ash from the total weight, it is necessary to subtract from this result the amount of iron (as Fe_2O_3) already found by the permanganate method, and the difference between the two results will show the amount of alumina existing in the sample; for in the former method the iron by itself was estimated, and in the latter the amount of $Fe_2O_3 + Al_2O_3$. To estimate the amount of calcium salts present, the filtrate mentioned above is raised to the boil, a little more ammonium hydrate is added, and a few cc. of a saturated solution of ammonium oxalate. The whole is well boiled for ten minutes, and if any calcium salt is present, it will be indicated by a white precipitate. This is carefully filtered on to a Swedish filter-paper, the precipitate being well washed on the filter, and the whole then placed in an air-bath to dry. When this is accomplished, the precipitate is ignited in a platinum crucible, the filter-paper being ignited before the bulk of the precipitate is added, and the whole is heated over the blowpipe for fifteen minutes. The result after deducting the weight of the crucible and ash will give the amount of calcium salt as oxide, contained in the original sample, and from this it will be necessary to calculate the oxide into sulphate, as it was doubtless present in that form in the sample, and in this connection it may be stated that 56 parts of CaO are equal to 172 parts of $CaSO_4 + 2\,H_2O$ (gypsum).

If the sample under examination is suspected to contain magnesium compounds, the filtrate from the last operation, which has been carefully preserved, is boiled down in a flask to reduce its bulk somewhat. It is then cooled, placed in a large beaker, and rendered alkaline by the addition of ammonium hydrate, after which about 50 cc. of a saturated solution of sodium phosphate are stirred in. The beaker is allowed to stand overnight, as the precipitate often takes a long time to form, and in the morning it is carefully filtered on to a Swedish filter-paper, the precipitate being then well washed with distilled water, to which has been added a little ammonium hydrate. The filter-paper and its contents are then set aside to dry, and ignited in a platinum crucible in the ordinary way. The precipitate now in the crucible has a composition represented by $Mg_2P_2O_7$, and after deducting the weight of the crucible and filter ash from the total weight, the amount of oxide or carbonate of magnesia present in the original sample is readily calculated from the above formula.

With regard to the amount of moisture present in oxides of iron, the estimation of such is a simple matter. Weigh out carefully 5 or 10 grammes upon a watch-glass, and dry in an air-bath heated to about 110° C., until no further loss in weight is noticed. This loss in weight represents the amount of moisture present in the sample, and, if it is desired to proceed a step further, and estimate the amount of combined water in the sample, a fresh lot of 5 or 10 grammes is weighed out in a platinum crucible, and the whole heated over a Bunsen burner for about an hour, when the loss in weight, minus that of the moisture, will indicate the amount of combined water in the sample.

In reference to the presence of such impurities as indicated, in a sample of oxide of iron, no hard and fast line can be laid down, and the judgment of the operator will be called into requisition as he is generally aware of the specific purpose for which the sample is intended. In this, as in all other cases, the question of cost is a prime factor; and if two samples were offered at the same price, one being practically pure, and the other containing 20 per cent. of a foreign body—which could be purchased at a cheaper rate than oxide of iron—the latter sample would be rejected without hesitation. For the purpose of reference, it may be stated that George H. Hurst, F.C.S., gives in his work on *Painters' Colours, Oils and Varnishes* a series of twelve complete analyses of samples of oxide of iron, which shows at a glance the composition of such articles now upon the market, and in which the percentage of Fe_2O_3 varies from 98 to 5 per cent.

POTASSIUM COMPOUNDS.

Under this classification the substances most frequently used in the colour works are potassium carbonate, or, as it is better known, pearl-ash or potash, and potassium hydrate or caustic potash, but they are frequently replaced by the cheaper and corresponding sodium compounds. The analysis for the largely used salt known as potassium bichromate, as well as that of the corresponding sodium bichromate, will be described at length under the heading of chromium compounds.

The first essential in the analysis of either potassium carbonate or hydrate is the preparation of a standard solution of sulphuric acid, which is made as follows:—

Forty-nine grammes of perfectly pure sulphuric acid are weighed out in a tared beaker, and the solution is made up to 1000 cc. in a standard flask. This solution must be standardised before use to ascertain its exact strength. For this purpose we dissolve 1·06 grammes of pure anhydrous sodium carbonate in distilled water in a white porcelain basin, and add a few drops of a solution of methyl-orange which acts as an indicator of the end of the reaction. The solution of sulphuric acid is now run into the basin slowly by means of a burette, until after stirring the contents of the basin by means of a glass rod, the original orange tint gives place to a faint and delicate pink. If the acid solution is exactly of the right strength, 20 cc. of it will be required, in which case 100 cc. of the standard solution will equal 6·9 grammes of potassium carbonate (K_2CO_3), 5·6 grammes of potassium hydrate (KHO), or 4·7 grm. of potassium oxide (K_2O).

Having obtained our standard solution of a known strength, the analysis of the sample is undertaken as follows :—

Weigh out carefully 10 grammes of the sample, which may be either the carbonate or hydrate, and dissolve in distilled water in a 500 cc. flask. From this made-up solution measure out by means of a pipette 250 cc., place in a white porcelain basin, add a few drops of methyl-orange solution, and titrate as already described with the standard sulphuric acid solution. When the faint pink colour is noticed, the number of cc. required to effect such a change is read off from the burette ; and, as every 100 cc. corresponds to either the amount of carbonate or hydrate already given, the calculation of the percentage in the sample under examination is an easy matter.

If a very exact analysis of the amount of available potassium salt in the sample is required, the above method will not suffice, for potassium salts frequently contain varying amounts of sodium salts, and both would be estimated together by the above process, and to overcome this we are compelled to resort to a more lengthy and expensive gravimetric operation as follows : Weigh out 5 grammes of the sample, and dissolve in distilled water, filter the solution to get rid of any insoluble matter ; and, after washing the filter-paper thoroughly with boiling distilled water, the solution is made up to 500 cc. in a standard flask. Measure out 25 cc. of this made-up solution by means of a pipette, place the liquid in a porcelain basin, and render the whole slightly acid by the addition of hydrochloric acid. A large glass should cover the basin during this addition, to prevent any loss from effervescence which will naturally occur in the presence of carbonate—the under side of the glass being washed into the basin afterwards. An excess of platinum chloride is now added, and the solution in the basin should remain of a yellow tint during the ensuing operation of evaporation; but, should it become colourless, more platinum chloride solution must be added until the yellow tint remains. The solution in the basin is evaporated almost to dryness, and a mixture of equal parts of alcohol and ether is added when the basin and its contents are quite cold. The precipitate will settle to the bottom of the basin, and the clear top liquor is filtered off through a small filter-paper. The precipitate is then washed with more alcohol and ether—the operation being repeated several times until the filtrate is quite colourless—then the small amount (if any) of the precipitate on the filter-paper is washed back into the basin which contains the greater bulk of the precipitate, and the whole is washed carefully into a tared platinum capsule, the contents of which are evaporated to complete dryness in an air-bath heated up to 105° C., and when thoroughly dry it is weighed. After deducting the original weight of the capsule from the result, and bearing in mind that the precipitate so obtained has a composition represented by the formula K_2PtCl_6, and that every 487 parts of it are equal to 138 parts of K_2CO_3, the calculation of the amount of potassium salt in the sample is an easy one. This method, owing to the use of the expensive platinum chloride and the length of the operation, is one only required in exceptional cases, and as a general rule the titration process with standard acid will furnish results sufficiently accurate.

SODIUM COMPOUNDS.

Under this heading we find that there are three substances largely used in all colour works. They are sodium carbonate, sodium hydrate or caustic soda, and sodium sulphate. The former comes into commerce under several names, such as soda-ash, pure alkali, sodium carbonate crystals, and the degree of purity varies greatly according to the process of manufacture. Sodium hydrate, or as it is more commonly called, caustic soda, is generally found as a hard rock-like substance usually packed in air-tight drums, for it has the power of absorbing moisture from the atmosphere, and hence is known as a deliquescent substance. It is also found in small lumps or powder, in which forms it is of greater utility to the general user, but the price is somewhat higher than that of the solid form. Sodium sulphate occurs in commerce in the form of crystals which are readily soluble in water, and are largely used for the formation of lake bases.

The valuation of sodium compounds is based upon the amount of available alkali present, except in the case of sulphate of soda crystals which is a neutral salt, and in this case an estimation of the amount of sulphate present is necessary.

The analysis of either sodium carbonate or hydrate is conducted upon exactly the same lines as those given for the corresponding potassium salts, but the factors representing the strength of the standard sulphuric acid solution are rather different for the sodium compounds. Soda-ash, or pure alkali, is represented by the chemical formula Na_2CO_3, and 100 cc. of the standard acid solution corresponds to 5·3 grammes of Na_2CO_3 or 3·1 grammes Na_2O. Sodium carbonate crystals, on the other hand, are represented by the formula $Na_2CO_3 + 7\ H_2O$, and consequently contain less available alkali weight for weight than the corresponding anhydrous compound. Caustic soda is represented by the formula NaOH, and consequently 100 cc. of the standard acid solution are equal to 4 grammes NaOH.

In the ordinary laboratory it is but rarely that anything more than an estimation of available alkali is required, as from this result the value of the sample can be accurately judged, but as sometimes samples of soda-ash are met with which contain varying amounts of insoluble matter, the following process for its estimation can be followed: Weigh out 50 grammes of the sample, dissolve in boiling distilled water in a beaker and allow the insoluble matter to settle. The contents of the beaker are then filtered through a Swedish filter-paper, and when all the insoluble matter has been transferred to the paper, the whole is well washed with boiling distilled water, until free from alkali, which is indicated by red litmus paper ceasing to turn blue. The filter-paper and its contents are then placed in the air-bath to dry, and afterwards ignited in a tared crucible; when, after deducting from the total weight that of the crucible + filter-paper ash and multiplying the result by 2, we have the amount of insoluble matter contained in 100 grammes of the sample, and this is rarely found to exceed 1 per cent.

As a guide, it may be stated that very pure brands of both carbonate and caustic-soda are now regularly placed on the market, in which the amount of available alkali expressed as carbonate or hydrate rarely falls below 98 per cent.

Sulphate of soda crystals $Na_2SO_4 + 10\ H_2O$ are examined as follows for the amount of sodium sulphate they contain, which in a perfectly pure sample is almost 44·1 per cent., but care must be taken in sampling the contents of a cask or bag, as this salt dries somewhat on exposure, which loss of the water of crystallisation consequently increases the proportion of sodium sulphate present.

Weigh out 5 grammes and dissolve in a flask or beaker by means of distilled water. Heat the solution to the boil, then add just sufficient pure hydrochloric acid to acidify, and then add slowly sufficient of a saturated solution of barium chloride to precipitate completely. The boiling is continued for several minutes, as by this means the precipitate assumes a more granular condition, and is then more easily filtered. The contents of the flask or beaker are then washed carefully on to a Swedish filter-paper—preferably of the ribbed pattern—and the whole is well washed with boiling distilled water until the filtrate is quite free from soluble salts. The filter-paper is then put to dry, and is afterwards ignited in the ordinary manner in a tared porcelain or platinum crucible, and bearing in mind that the precipitate so obtained is barium sulphate ($BaSO_4$), the calculation into the equivalent of sodium sulphate is a simple matter, as 233 parts of the precipitate correspond to 80 parts SO_3, and 322 parts of $Na_2SO_4 + 10\ H_2O$. If the sodium compounds are intended for the production of Madder lakes, it will be necessary to test them for the presence of iron, which is carried out in a similar manner to the method given under aluminium compounds; and, if any is detected, the sample must be rejected, as it will be impossible to produce a bright result with such an impurity.

AMMONIUM HYDRATE.

This is practically the only product under ammonium compounds which is put to an extended use in colour works. It is the well-known ammonia of commerce, and is always recognised by its pungent and penetrating odour. It is usually found in a high state of purity, with a specific gravity of 0·880 and containing about 30 per cent. of NH_3. The valuation of samples is usually performed by carefully ascertaining their specific gravity, and comparing the same with the elaborate tables found in any standard work, and which indicate at a glance the percentage of available NH_3 present. If a direct estimation is desired, the standard sulphuric acid solution is again called into requisition; and, after weighing out 25 grammes of the sample, and making up to 500 cc. in a standard flask, 50 cc. are withdrawn by means of a pipette and transferred to a white porcelain basin, to which a few drops of methyl-orange solution are added. The standard acid solution is then added slowly from a burette, until the solution in the basin turns to a faint pink after stirring, which change indicates the end of the reaction. The number of cc. of acid required to produce this is noted, and as 100 cc. of it are equal to 1·7 gramme NH_3 the calculation to express the percentage contained in the sample is simple and straight forward.

ACIDS.

The acids in common use in colour works are sulphuric acid, commonly known as oil of vitriol, which is represented by the formula H_2SO_4; hydrochloric acid, also known as spirit of salts or muriatic acid, and represented as HCl; nitric acid or *aqua fortis*, HNO_3, and acetic acid, which is represented by the formula $C_2H_4O_2$. The first three belong to the inorganic, and the latter to the organic classification of substances. Each of these differs materially from the others in its properties, mode of preparation, and the uses to which it is put—but all are useful to the colour-maker in many ways.

In each case the value of a sample is judged by the amount of available acid it contains: the higher the amount the purer the sample; and the method of estimating this important factor is the same for each, and consists of neutralising the acid with a standard alkaline solution in the presence of an indicator.

To prepare the requisite standard alkaline solution we proceed as follows: Weigh out carefully 40 grammes of perfectly pure caustic-soda, which is sold for such purposes by any firm supplying laboratory requisites, and dissolve the same in a litre (1000 cc.) of distilled water. When this is accomplished, the solution must, for the sake of accuracy, be standardised against the sulphuric acid solution—made as described under the analysis of potassium compounds—and if the solution is of the proper strength, 20 cc. will require exactly the same amount of the standard sulphuric acid solution to neutralise it, and the end of the reaction is plainly seen when the methyl-orange, added as an indicator, turns to a faint pink tint after the contents of the vessel in which the titration is performed have been stirred by means of a glass rod. Assuming, then, that the standard caustic soda solution is of the proper strength, it will correspond to the above acids in the following extent:—

100 cc. Standard NaOH solution =	4·9 grammes	H_2SO_4.
	3·65 ,,	HCl.
	6·3 ,,	HNO_3.
	6·0 ,,	$C_2H_4O_2$.

Sulphuric Acid.

A careful determination of the specific gravity of a sample of this acid will indicate its approximate strength when the result is compared with the published tables which show the percentage of acid contained in samples of various densities. By reason of their length, the tables cannot be given here; but they are found in most works of reference, and are often a valuable aid to the chemist.

To determine accurately the percentage of available acid in any sample, it is necessary to weigh out carefully 50 grammes, and dilute the same to a litre (1000 cc.). From this made-up solution 25 cc. are measured off, preferably by means of a burette, into a porcelain basin, and after adding sufficient distilled water to make a workable quantity, the whole is titrated with the standard caustic soda solution, using methyl-orange as an indicator, and stirring the contents of the basin continually whilst the standard solution is being added. The end of the reaction is perceived by the pink shade of the solution changing to orange, and by noting the amount of standard solution required to produce this change; and, bearing in mind its equivalent in sulphuric acid, the calculation to express the percentage of H_2SO_4 in the sample becomes one of simple multiplication. As a guide it may be stated that the purest sulphuric acid of commerce is known as rectified oil of vitriol, and whilst it shows at 60° Fahr. a specific gravity of 1·840, it usually contains about 95·6 per cent. of sulphuric acid.

The impurities present in commercial samples of this acid will vary in extent and nature, according to whether the sample has been manufactured from pyrites or sulphur—the latter being always the purer product. Such impurities may consist of any or all of the following substances: sulphates of lead, iron, soda and arsenic—especially in acid made from pyrites. With the exception of arsenic, these are usually neglected, but if the acid enters into the composition of any bases intended for use in the paper-staining trade, it will be advisable to reject any samples containing arsenic, as paper-stainers are very particular in refusing to accept any lakes as pigments which contain such an objectionable impurity.

To detect arsenic we proceed as follows: Measure out about 50 cc. of the sample under examination, dilute with about 500 cc. of distilled water in a beaker, then allow a stream of sulphuretted hydrogen gas to bubble through the liquid for about 10 minutes. A yellow precipitate will indicate the presence of arsenic, and to further confirm this, the precipitate is allowed to settle, the top liquor poured away, and the precipitate is then dissolved in a solution of ammonium carbonate, in which arsenious sulphide is soluble. The result can be confirmed either by the Reinsch or Marsh tests, which are described in detail under the consideration of arsenic compounds.

Hydrochloric Acid.

This acid usually appears in commerce with a specific gravity of 1·16, and containing about 32 per cent. of available HCl. It is generally of a straw colour, owing to the presence of iron and organic impurities, which are however usually small in amount and of little importance. The specific gravity of a sample is usually a good guide as to its strength, and tables are usually found in all works of reference which indicate the amount of acid for each degree of specific gravity. If it is desired to obtain a more accurate estimation of the amount of available acid present, the following process can be followed:—

Weigh out 50 grammes of the sample, and dilute the same up to 1 litre with distilled water. From this made-up solution measure out—preferably by means of a burette—100 cc. into a white porcelain basin, and using methyl-orange as an indicator, titrate with the standard caustic soda solution in exactly the same manner as already described under sulphuric acid, and calculate the result from the factor given.

Nitric Acid.

This product does not find such extended uses in the colour works as the two acids already considered. It is usually found fairly pure, and generally has a specific gravity of 1·325 which represents about 51 per cent. of HNO_3. The specific gravity of a sample is usually a reliable index as to its strength, which can be obtained by reference to the published tables, but if a more accurate determination be desired the process for the determination of hydrochloric acid is followed in detail as given.

The presence of sulphuric and hydrochloric acids will indicate an adulterated sample, and to detect such it is necessary to dilute the acid with about twice its bulk of distilled water, and to divide the solution into two portions. To one of these a few drops of barium chloride solution are added, when a white precipitate will indicate the presence of sulphuric acid; and to the other a few drops of silver nitrate solution are added, when a white curdy precipitate indicates the presence of hydrochloric acid. Should any sample of nitric acid indicate the presence of either or both of these impurities it should be rejected, as it is easily possible to obtain commercial samples which are free from such contamination, or which at the most show only faint traces.

Acetic Acid.

The specific gravity of this acid offers no reliable indication as to the amount of available acid it contains, and the estimation of its strength is always ascertained by a direct titration with the standard caustic soda solution, but in this case a few drops of phenolphthalein solution form the indicator. This substance has the property of remaining colourless in acid or neutral solutions, but assumes a rose colour with a very faint trace of free alkali. The titration is carried out exactly as described for hydrochloric acid with the above exception, and until the liquid in the basin assumes a faint pink tint, which indicates the end of the reaction.

Commercial samples of this acid are liable to be contaminated with sulphuric and hydrochloric acids or their corresponding salts, and the presence of such can be detected by the methods given for the detection of similar bodies in nitric acid.

CHROMIUM COMPOUNDS.

Under this heading the most important substances used by the colour-maker are sodium bichromate ($Na_2Cr_2O_7 + 2H_2O$) and potassium bichromate ($K_2Cr_2O_7$). As these substances enter into the composition of all chrome yellows, it will be seen that they are important articles of commerce, and fortunately for all concerned they come upon the market in a state of fair purity and regular composition. The cheaper sodium salt has almost entirely replaced the potassium compound in general use, as it gives identical results and contains practically the same amount of CrO_3 (the oxide corresponding to chromic acid), the exact figures being 67·7 per cent. in the case of the sodium, and 68·09 in that of the potassium salt. There is one difference, however, between these two salts which should always be borne in mind, for whilst the sodium variety has the property of absorbing atmospheric moisture very rapidly, the potassium compound does not, hence it is always necessary to keep the former away from atmospheric influence when not actually in use. On the other hand, the former dissolves more readily in water than the latter, and usually at a lower temperature, which is often a great advantage.

The value of either of these compounds depends upon the amount of CrO_3 they contain, and in order to estimate this, the following process is recommended, as but little practice is required to master the necessary details :—

Weigh out 5 grammes of the sample under examination, and dissolve in distilled water, making the solution up to 1000 cc. A burette is then filled with a portion of the solution, and 1 gramme of ammonium ferrous sulphate is dissolved in distilled water in a white porcelain basin. A white porcelain plate is then dotted over with separate drops of a solution of potassium ferricyanide. The solution in the basin is then slowly titrated with the solution in the burette, until—after stirring—a drop taken from the basin by means of a glass rod, and brought in contact with one of the drops of ferricyanide solution upon the plate, ceases to give a blue or greenish-blue coloration. The reaction is then complete, and the number of cc. of the solution in the burette required to produce this change is noted, and for the sake of illustration we will presume that the amount so required was 25·5 cc. As 1 gramme of the ammonium ferrous sulphate reduces 0·0854 grammes of CrO_3, it will be evident that 25·5 cc. of the solution in the burette is equal to that amount. Therefore, if we multiply 0·0854 by 1000, and divide by 25·5 we obtain the amount of CrO_3 in the 5 grammes of the sample we originally weighed out; and by multiplying this result by 20 we obtain the percentage of CrO_3 in the sample under examination, and the result will be found to be 66·98 per cent.

A gravimetric process may also be followed for the estimation of CrO_3, and is carried out as follows:—

Five grammes of the sample are dissolved in 1000 cc. of distilled water, and 100 cc. of this made-up solution are measured into a beaker. A little hydrochloric acid is then added, and the whole heated with alcohol or sulphurous acid. The liquid is boiled until it ceases to smell of alcohol or sulphurous acid, at which point it is diluted to about twice its bulk with distilled water, and it will now be noticed that the solution is green in colour. Ammonium hydrate is now added in excess, which causes a precipitate to form, and this is carefully filtered off on to a Swedish filter-paper, where it is well washed with boiling distilled water. It is then dried in the air-bath, and ignited in the usual way in a tared crucible, the weight of which plus that of the filter-paper ash being deducted from the total weight. The precipitate so obtained has the compositions Cr_2O_3, and in calculating our results we must bear in mind that 153 parts of Cr_2O_3 correspond to 201 parts of CrO_3.

Still another gravimetric method may be followed for the estimation of CrO_3 in bichromates, and it depends upon the conversion of the sample under examination into lead chromate or chrome yellow. Ten grammes of the sample are dissolved in distilled water, and made up to 500 cc. in a standard flask. Take out 50 cc. of this solution, place in a beaker, and add 20 cc. of pure acetic acid. Heat the contents of the beaker to about 80° C., and then precipitate with a solution of pure lead acetate. A yellow precipitate, which is lead chromate ($PbCrO_4$) will immediately form; this is allowed to settle, and is then carefully washed on to a Swedish filter-paper. The washing must be done thoroughly with hot distilled water to get rid of all soluble salts, and the filter and its contents are dried in the air-bath at a temperature of about 105° C. The precipitate is then ignited at a dull red heat in a tared porcelain crucible, which after cooling is weighed. After deducting the weight of the crucible and filter-paper ash from the total weight, the result gives the amount of $PbCrO_4$ yielded by 1 gramme of the original substance, and as 323·5 parts of this precipitate are equal to 100·5 CrO_3, the remaining calculation is easy.

TIN COMPOUNDS.

The use of these compounds in the colour works is not extensive, and is confined almost entirely to the production of the so-called "Wood Lakes," which are prepared from solutions of the colouring principle contained in the numerous dye-woods and barks of commerce. These lakes, unfortunately, are not as well known in the trade as they should be, for the amount of "body" and consequent covering power which they possess causes them to rank very high, but owing to the various processes required in their manufacture, the prices rule somewhat high, and on this account alone they are relegated into the background.

The two compounds of tin used in the above connection are stannous chloride and oxy-muriate. The former comes into commerce either in the form of crystals, in which case it has a composition represented by $SnCl_2 + 2\ H_2O$, or as a solution usually with a specific gravity of 1·60. Commercial samples of stannous chloride crystals, or tin crystals as they are generally called, usually contain from 50 to 51 per cent. of available tin, and a solution of the above specific gravity, which is generally known as muriate of tin, should contain, if pure, about 23 per cent. of tin. Oxy-muriate of tin is a liquid usually sold with a specific gravity of 1·60, and it differs considerably from muriate of tin, inasmuch as the tin which it contains has been converted from the stannous into the stannic condition by oxidation with nitric acid. A good sample should be free from suspended matter and an excess of free acid, and should show a characteristic golden fluorescence.

As the value of all tin compounds is judged by the amount of available tin which they contain, the following processes for its estimation can be followed :—

Weigh out 2 grammes of the stannous compound in either its solid or liquid form, add 25 cc. of a saturated solution of pure ferric chloride and 2 cc. of pure hydrochloric acid, and make the solution up to 500 cc. with distilled water in a standard flask. Measure out by means of a pipette 100 cc. of this made-up solution, placing the same in a white porcelain basin which is already half-filled with freshly boiled and cooled distilled water. This is titrated with a standard solution of potassium permanganate (100 cc. of which equals 0·59 gramme of tin) until the whole retains a very faint pink tint after stirring. The reaction is then complete, or, in other words, the stannous salt has become oxidised into the stannic condition by oxygen absorbed from the permanganate. For the sake of accuracy, it is advisable to measure out 25 cc. of the ferric chloride solution and 2 cc. of hydrochloric acid; make the liquid up to 500 cc. with distilled water, then take out 100 cc. and titrate in the manner described above, in order to see whether this solution acts upon the permanganate. When this is the case the amount of permanganate required is usually very small, but it must be deducted from the total used in the first experiment, and the amount of stannous salt in the sample is calculated from the data obtained. Thus as an illustration it may be assumed that, working with crystals, our first titration required 35 cc. of the permanganate solution, and the second, or blank experiment, required only 0·1 cc., which shows that 34·9 cc. of permanganate was required by the tin in the solution. If we multiply this figure by 250 we shall obtain the number of cc. of the standard solution required by 100 grammes of the original sample, and as every 100 cc. of the same corresponds to 0·59 gramme of tin, we find the percentage of available tin in the sample under examination to be 51·47.

In the case of oxy-muriate, as already shown, the tin exists in the stannic or oxidised condition, and the above process cannot be followed. We must resort to a gravimetric process which is conducted as follows: Weigh out carefully 2 grammes of the sample, place into a beaker, add about 100 cc. of distilled water, heat to the boil, and boil briskly for about fifteen minutes, at the end of which period all the tin will have been precipitated. This is allowed to settle, and is then carefully washed on to a Swedish filter-paper, and afterwards dried in the air-bath. When thoroughly dry it is ignited in a porcelain crucible in the usual manner, and after deducting from the total weight that of the crucible and filter-paper ash, we obtain the amount of stannic oxide (SnO_2) yielded by 2 grammes of the original sample, and bearing in mind that 150 parts of this compound contain 118 parts of tin, the necessary calculation is soon made. As a guide it may be stated that a good sample of oxy-muriate will yield about 29 per cent. of stannic oxide, which is equivalent to 22·8 per cent. of tin.

Tin compounds now appear upon the market in a very pure form compared with what was the case a decade ago. This is owing to the keen rivalry between manufacturers in supplying the enormous demands of the dyeing and calico-printing industries, and indirectly the colour-maker reaps the benefit. Formerly varying quantities of zinc and magnesium sulphates, and even zinc chloride were largely used to adulterate tin crystals, and muriate of tin solutions often contained appreciable quantities of sodium chloride. Should the percentage of tin found in the sample under examination fall much below the figures given, the above impurities should be tested for, and if found the sample should be rejected.

Sulphates of zinc or magnesia can be detected by the addition of hydrochloric acid and barium chloride to the solution, a white precipitate indicating the presence of either or both. To differentiate between zinc or magnesia, a portion of the original substance is dissolved in distilled water, and made slightly acid with hydrochloric acid. Through this solution a current of sulphuretted hydrogen gas is allowed to bubble briskly for about fifteen minutes, and the tin sulphide so obtained is filtered off, after which the filtrate is boiled until it ceases to smell of sulphuretted hydrogen, then cooled, rendered alkaline with ammonium hydrate, and a few drops of ammonium sulphide added. A white precipitate which usually takes some time to form and settle indicates zinc. This is filtered off, and the filtrate again boiled to a small bulk, when it is cooled, rendered alkaline with ammonium hydrate and a small quantity of sodium phosphate solution added. The liquid is stirred well with a glass rod and allowed to stand overnight, after which a white, almost crystalline precipitate will settle out if magnesia was present in the original sample.

COPPER COMPOUNDS.

From the point of view of a colour-maker these compounds are not important, and we find that copper sulphate $CuSO_4$, 5 H_2O is the only one used to any extent, but in view of the recently published processes for making lakes with the Diamine series of coal tar products, its use in the near future is likely to become largely extended.

The value of copper sulphate, or, as it is often called, bluestone, or blue-vitriol, depends upon the amount of available copper it contains, and it is found in commerce in the form of well-defined blue crystals which are usually free from intentional adulteration. A small quantity of ferrous sulphate is almost invariably found even in the best brands, but the amount is usually very small, and is due to the difficulty of entirely eliminating iron during the manufacturing process.

Except in very extreme cases an estimation of the amount of copper present in the sample is all that is required, and the method of procedure is as follows: Weigh out carefully 1 gramme of the powdered sample, place in a porcelain basin, and add about 250 cc. of distilled water. Heat up gently to the boil, and then stir in an excess of a solution of pure caustic soda or potash, until all the copper is precipitated. Set the basin aside to cool, and as the precipitate will have settled down, it can be readily washed two or three times by decantation, or until the washings are free from alkali, which is indicated by red litmus paper ceasing to turn blue. The precipitate is then washed on to a Swedish filter-paper, and afterwards dried in the air-bath. Before ignition the precipitate is carefully separated from the filter-paper, and then ignited in the usual way over a Bunsen flame without using the blowpipe. The crucible is then cooled under a dessicator, and after deducting from the total weight that of the crucible and filter ash, we obtain the amount of copper oxide (CuO) yielded by 1 gramme of the original substance, and in calculating the results to percentage, it must be remembered that 79 parts of the precipitate so obtained correspond to 63 of metallic copper or to 249 parts of copper sulphate in the crystallised condition. As a guide it may be stated that 100 parts of pure crystallised copper sulphate contain 25·3 parts of metallic copper.

The manufacture of various copper blues, formerly an extensive business, is now only followed to a limited extent by a few firms. As it is sometimes necessary to distinguish rapidly between such a blue and imitations, the following tests can be applied to any sample, as they serve to distinguish between colours containing copper, and those free from it. On heating in a porcelain crucible, any blue containing copper will darken in colour, owing to the formation of black oxide of copper. Should this indication be masked by the presence of other ingredients, a small portion of the sample is boiled with dilute nitric acid, which dissolves any copper present. The liquid is filtered and the filtrate divided into two equal portions. To one of these an excess of ammonium hydrate is added, when, if copper is present, a deep blue coloration will be observed. To the other portion of the solution a few drops of potassium ferrocyanide solution are added, when a deep brown precipitate will indicate the presence of copper.

Copper greens, of which there are many varieties, have also in late years given way before the introduction of more suitable pigments. Any green suspected to contain copper will answer to the same tests as the copper blues.

LEAD COMPOUNDS.

The use of these compounds in paint and colour works is universal, and judging from the present high prices of the same, the demand is a growing one. Broadly speaking, they may be divided into two classes—soluble and insoluble—in regard to their behaviour with water, and under the first division we encounter lead acetate or white sugar of lead, $Pb(C_2H_3O_2)_2 + 3H_2O$, which now enters commerce containing about 99 per cent. of the crystallised salt; brown sugar of lead, which is a less pure form made from impure acetic acid, and containing usually about 90 per cent. of the crystallised salt; and lead nitrate $Pb(NO_3)_2$ which is now placed upon the market in a high state of purity. Amongst the insoluble lead compounds we have the basic carbonate of lead or white lead, $2\,PbCO_3Pb(OH)_2$, which from the excellence of its body and covering power enters so largely into the composition of white and other paints; and the various oxides of lead which from their shades are known respectively as red and orange leads. We also occasionally come across lead sulphate, $PbSO_4$, which enters into the composition of paints, and thus it will be seen that lead compounds are an important item in the works, entering as they do in the paint department into so many mixtures, and in the colour department into permanent and Madder Reds, vermilionettes and other colours, including chrome yellows, Brunswick greens, etc.

Whether belonging to the soluble or insoluble variety, their value is judged by the percentage of available lead they contain, and in the case of the soluble salts this is ascertained as follows :—

Weigh out carefully 1 gramme of the sample, place in a beaker, and dissolve in about 200 cc. distilled water. When the solution is complete, add sufficient pure acetic acid to render it decidedly acid, and heat up to about 80° C. Sufficient of a solution of pure bichromate of potash is then added to precipitate all the lead as chromate, and when this is accomplished the beaker is set aside for the precipitate to settle. It is then collected on a dry, tared Swedish filter-paper, washed free from soluble salts with hot distilled water, and dried thoroughly in the air-bath at a temperature not exceeding 105° C. and then weighed. After deducting from the total weight that of the filter-paper, we obtain the amount of lead chromate ($PbCrO_4$) yielded by 1 gramme of the sample, and from the figures so obtained we can readily calculate the amount of lead or lead oxide (PbO) contained in 100 grammes of the sample, bearing in mind that 323·5 parts of $PbCrO_4$ contain 207 parts of Pb, or 223 parts PbO.

The lead oxide compounds insoluble in water are examined differently, and after weighing out 1 gramme of the sample it is dissolved at the boil with a mixture of pure dilute nitric and hydrochloric acids. When the solution is complete, any insoluble matter present is filtered off, and the cold solution is placed in a porcelain basin, and evaporated carefully to a small bulk. This liquid is cooled and diluted with about three times its bulk of absolute alcohol, after which about 20 cc. of pure sulphuric acid are added. The whole is now well stirred with a glass rod and heated up to about 90° C., when a heavy, white precipitate of lead sulphate will settle out. The solution is again cooled, and then carefully filtered through a Swedish filter-paper, upon which the precipitate is washed (until free from acid) by absolute alcohol. The filter-paper and its contents are then dried in the air-bath, and afterwards ignited in the usual manner in a tared porcelain crucible. From the figures so obtained we have the amount of lead as sulphate in 1 gramme of the sample, and as 303 parts of the precipitate correspond to 207 parts of Pb, or 223 parts PbO, the remaining calculation is easy and straightforward.

There are many other methods for the estimation of lead in soluble or insoluble compounds, but for all practical purposes those given will suffice, and it is but seldom that the chemist in the average laboratory is called upon to do more than estimate the amount of lead contained in any sample; for, thanks to keen competition in this and continental countries, the makers now supply products of excellent purity, although it must be admitted that in the cases of the red and orange varieties they appear unable to deliver two lots exactly alike in shade and purity of tone, and, sadder still, the same cask will often contain two distinct shades. This is greatly to be deplored, as manufacturers of vermilionettes and Madder Reds know to their discomfort, and when this difficulty is satisfactorily overcome, the manufacturers of lead products can congratulate themselves upon turning out a set of raw materials as pure and reliable as those of any other branch of chemical manufacture.

ZINC COMPOUNDS.

Under this heading several white pigments are largely used in paints, and are sold as such under a variety of fancy names. The principal ingredients found in such mixtures are the oxide of zinc ZnO, and the sulphide ZnS, and varying proportions of barytes are added for the sake of cheapness. The oxide when pure is generally known as zinc or Chinese white, but the sulphide is rarely found in such a condition. Occasionally the colour-maker uses the oxide as a base by itself or admixed with other suitable ingredients, but owing to its great power of absorbing colour, and poor body, it is not in favour for such purposes.

Either of the substances mentioned above, or any mixture containing one or both, is judged for value by the amount of zinc which it contains, and the estimation of such presents no difficulties to the ordinary operator, but owing to the fact that the impurities present may consist of china-clay, gypsum and barytes, the examination of a sample is a somewhat lengthy process.

For the analysis it is necessary to weigh out 5 grammes of the sample, which is placed in a beaker and dissolved in pure hydrochloric acid. It should dissolve readily, without effervescence and without leaving any residue if quite pure. If any effervescence is noticed it indicates the presence of carbonates as an impurity, and such may consist of either white lead, whiting, or magnesium carbonate, or all three. If any residue remains, it may indicate either china clay or barytes, and if the acid solution is yellow in colour it indicates the presence of iron. When the solution is complete any residue is filtered on to a Swedish filter-paper, which is carefully washed until free from acid, and set aside for further examination, the washings and the original solution being carefully made up to 500 cc. in a standard flask. For the analysis 100 cc. of this made-up solution are measured out by means of a pipette and placed into a beaker, which is half-filled with distilled water. This is raised to the boil, and about 25 cc. of a saturated solution of ammonium chloride are added, after which the whole is rendered alkaline with ammonium hydrate. At first a white precipitate will be formed, which will dissolve in an excess of the latter reagent; and, when this is accomplished, the boiling is continued for a few minutes, and the beaker is then set aside to cool. Should the well-known grey flocculent precipitate of aluminium hydrate appear, it will indicate the presence of china clay in the original sample, and by filtering the liquid through a Swedish filter-paper the precipitate will remain thereon, but it must be well washed until free from alkaline reaction and the washings added to the filtrate. The amount of Al_2O_3 present can then be estimated as already described under Aluminium Compounds. The filtrate is then placed in a tall beaker and sufficient ammonium sulphide solution is added to precipitate all the zinc present as sulphide. After stirring well the beaker is allowed to stand overnight, and in the morning the clear liquid can be drawn off by means of a syphon and kept for further examination. The precipitate is filtered on to a Swedish filter-paper and washed well with distilled water containing traces of ammonium hydrate and sulphide, the washings being added to the filtrate before mentioned. The filter-paper and its contents are then dried in the air-bath, and after separating the dry precipitate from the paper as completely as possible, the latter is ignited in a porcelain crucible, and when only a white ash remains the precipitate is added, and the crucible and its contents are heated over a Bunsen flame at a bright red heat for about fifteen minutes. The lid of the crucible should be removed during this operation, and free access of air permitted, as oxygen is required to get rid of the sulphur present. When the ignition is complete, the crucible and its contents are weighed, and after deducting the weight of the crucible and filter ash from the total weight, the result expresses the amount of ZnO yielded by 1 gramme of the sample; and as a guide it may be stated that a pure brand will yield not less than 98·5 or 99 per cent.

The filtrate from the above is now examined for such impurities as calcium and magnesia, but it will first of all be necessary to boil down the bulk somewhat. When this is done the liquid is made alkaline with ammonium hydrate and heated up to the boil, at which point about 25 cc. of a saturated solution of ammonium oxalate are added. A white precipitate indicates the presence of calcium, and if it is desired to estimate the amount present, the boiling should be continued for at least ten minutes, as by so doing the precipitate assumes a more granular form, and is easier to filter. The precipitate is filtered on to a Swedish filter-paper, and well washed with hot distilled water until free from soluble salts, the washings being added to the filtrate which is set aside for subsequent examination. The filter-paper and its contents are dried in the air-bath, and afterwards ignited in the usual manner in a tared platinum crucible at a bright red heat, the operation being finished with the blowpipe flame. After the crucible has cooled it is weighed, and after deducting from the total weight that of the crucible + filter-paper ash, we obtain the amount of CaO yielded by 1 gramme of the sample, and we can either calculate this into sulphate of lime (gypsum), $CaSO_4$, in which case 56 parts of CaO correspond to 136 parts $CaSO_4$, or 172 parts $CaSO_4 + 2H_2O$, or we can express the result as carbonate of lime (whiting), in which 56 parts CaO correspond to 100 parts $CaCO_3$.

To the filtrate from the above we add a further quantity of ammonium hydrate, and about 25 cc. of a saturated solution of sodium phosphate, and stir the mixture well, afterwards setting it aside overnight as the precipitate takes considerable time to form and settle. Any precipitate which is present in the morning indicates the presence of a magnesium compound as an impurity in the original sample, and it is carefully filtered on to a Swedish filter-paper, and well washed with distilled water containing traces of ammonium hydrate and sodium phosphate. It is then dried at about 100° C. in the air-bath, and ignited in the usual manner in a tared platinum crucible. The resulting substance has a composition represented by the formula $Mg_2P_2O_7$, and every 111 parts of the same are equal to 24 parts Mg, or 40 parts MgO, or 84 parts $MgCO_3$.

Assuming that at the commencement of the analysis the sample was not entirely soluble, the residue should now be examined as follows: After its weight and amount have been ascertained, a piece of platinum wire is heated in the Bunsen flame until it ceases to impart any colour, and it is then dipped into pure hydrochloric acid and then into the residue, a small portion of which will be transferred upon the wire. This is now held again in the Bunsen flame, to which a green coloration will be imparted if barytes is present. Should no coloration appear, or only the yellow of sodium be observed, the residue will in all probability consist of silica from china clay, but in this case alumina will have been observed as already described.

In rare cases white lead may be observed as an adulterant of zinc white, and if its presence is suspected, the test is made as follows: 100 cc. of the made-up solution are placed in a beaker and diluted with distilled water. A stream of sulphuretted hydrogen gas is allowed to bubble briskly through the liquid for about ten minutes, when a black precipitate of lead sulphide will indicate such contamination. The amount can be estimated by filtering off such precipitate, dissolving it in nitric acid, and precipitating with sulphuric acid as lead sulphate, in the manner already described under lead compounds.

When a number of samples of zinc oxide have to be examined with rapidity, the gravimetric process given for the estimation of zinc will be found tedious and lengthy, and the following volumetric method is given, as it is carried out with ease and rapidity, furnishing at the same time results of unquestionable accuracy, the only feature to be observed is that the samples are free from iron or copper. The first essential is a standard solution of pure potassium ferrocyanide crystals ($K_4FeCy_6 + 3H_2O$), and in order to obtain this 43·2 grammes of the salt are dissolved in 1000 cc. of distilled water. This solution is then standardised upon a known weight of pure zinc sulphate ($ZnSO_4 + 7\ H_2O$), as follows: Weigh out carefully 0·5 gramme of zinc sulphate, transfer to a flask and dissolve in distilled water. The solution is then rendered acid by the addition of pure dilute hydrochloric acid, and afterwards raised to the boil. Upon a white porcelain plate placed alongside of the flask several separate drops of solution of uranium acetate or nitrate are scattered. The liquid in the flask is now titrated with the standard solution until a drop taken out and transferred to one of the drops of uranium solution upon the plate gives a faint and delicate brown coloration. This indicates the end of the reaction, and as every 287 parts of pure crystallised zinc sulphate correspond to 65 parts of zinc, we can readily calculate the strength of the standard solution in reference to the amount of zinc to which it corresponds, and this important factor having been ascertained, it is carefully noted, for the standard solution so produced will keep for an indefinite length of time. If strictly accurate, 100 cc. of the standard solution will correspond to 1·0 gramme Zn. For the analysis, 0·5 gramme of the sample is weighed out, dissolved in pure dilute hydrochloric acid, boiled and titrated in the manner just described, and it will be at once evident that the estimation of zinc by this method becomes a matter of minutes instead of hours when the gravimetric process is followed.

MANGANESE COMPOUNDS.

The compounds to be noticed under this heading are used chiefly in the paint department in the form of "driers," although occasionally the black oxide MnO_2 is used in certain mixtures as a self-colour. For the manufacture of "driers," however, the manganese compounds usually used are the chloride $MnCl_2 + 4H_2O$, and the sulphate $MnSO_4 + 4\ H_2O$, as it has been found that the oxide alluded to is very powerful in its action, and has a strong tendency to darken any paint to which it is added. The two salts mentioned are found in commerce with a faint pink tint, and usually of fair purity. The value of any manganese compound is judged by the amount of manganese which it contains, and the estimation thereof presents no difficulties, the method of conducting the analysis being as follows: Weigh out carefully 1 gramme of the sample, place into a white porcelain basin, and dissolve in about 250 cc. of distilled water. When thoroughly dissolved, heat up to about 80° C., and add sufficient of a solution of pure caustic soda or potash, to precipitate fully. The basin with its contents is then set aside, and when the precipitate has settled, it is washed several times by decantation with hot distilled water, until quite free from alkali. The precipitate is then filtered on to a Swedish filter-paper, again washed, then dried in the air-bath at about 105° C., and afterwards ignited in a porcelain crucible in the ordinary way. After subtracting the weight of the crucible and filter-paper ash from the total weight, we obtain the amount of red manganese oxide Mn_3O_4 yielded by 1 gramme of the sample; and, in making the necessary calculation to obtain the percentage, it must be remembered that 229 parts of Mn_3O_4 correspond to 165 parts Mn.

In dealing with the black oxide of manganese MnO_2, it is first of all necessary to dissolve 1 gramme of the sample in hydrochloric acid, after which the process is carried out exactly as above described.

When several samples of MnO_2 have to be examined, a volumetric process can be followed, as it yields very accurate results in much less time than the gravimetric method already given.

This process depends upon the fact that several substances rich in oxygen decompose when heated with hydrochloric acid and evolve free chlorine in proportion to the amount of oxygen present. Thus when MnO_2 is heated with hydrochloric acid a decomposition represented by the following equation takes place:—

$$MnO_2 + 4\ HCl = MnCl_2 + Cl_2 + 2\ H_2O,$$

and consequently 71 parts of chlorine are equivalent to 87 parts of MnO_2, and if the chlorine so evolved is conducted into a solution of potassium iodide (KI) the chlorine will combine with the potassium, and free iodine will be liberated, the amount of which is then determined by titration with a standard solution of sodium hyposulphite ($Na_2S_2O_3$ + 5 H_2O).

The standard solution of hyposulphite is made by dissolving 25 grammes of the dried re-crystallised salt in distilled water, and making the solution up to 1000 cc. This solution must then be standardised upon the standard iodine solution to be described under the consideration of arsenic compounds, and should be of such a strength that 1 cc. of the hyposulphite solution exactly neutralises the same volume of the iodine solution.

The apparatus required is simple, and consists of a small flask connected by means of a bent glass tube and tightly fitting india-rubber corks with a U-tube, which is in turn connected with a second U-tube. These two tubes must be suspended in a large beaker, which is filled with cold water during the analysis.

For the purpose of the analysis, weigh out about 0·2 gramme of the sample, placing the same in the small flask, to which is then added about 25 cc. of strong hydrochloric acid. Into each of the two U-tubes place about 25 cc. of a cold saturated solution of potassium iodide, the object of the second U-tube being merely to absorb any chlorine which escapes from the first. When all is ready for the analysis, the small flask is gently heated by means of a Bunsen flame until its contents reach the boil, and the boiling is continued for about five minutes. It will be noticed that the solution in the first U-tube changes to a dark brown colour owing to the liberated iodine, and when the operation is concluded the contents of both U-tubes are washed with distilled water into a porcelain basin, but unless the solution in the second tube has darkened in colour it need not be so added.

The liquid in the basin is diluted somewhat with distilled water, and is then titrated with the hyposulphite solution until the colour of the iodine is almost destroyed. A few drops of a solution of starch in distilled water are now added, and the titration is continued until the blue colour formed by the addition of the starch entirely disappears. This completes the reaction, and as the strength of the hyposulphite solution has already been determined by titration upon the standard iodine solution in a similar manner, we have before us the equivalent in iodine of the hyposulphite solution, and bearing in mind that 100 cc. of the standard iodine solution corresponds to 0·355 gramme chlorine the resulting calculation is straightforward.

The following statement of figures obtained in an analysis will serve as a useful guide: 0·174 gramme MnO_2, treated as described above, required 26·2 cc. of standard hyposulphite solution of such a strength that 100 cc. corresponded to 0·355 gramme Cl.; therefore, as according to the equation 71 parts of Cl. correspond to 87 parts of MnO_2, the percentage of MnO_2 in the sample under examination was 65·49.

ARSENIC COMPOUNDS.

In the colour works arsenic in the form of arsenious acid As_2O_3 is still largely used for the manufacture of a body or base, which possesses covering powers superior to any other. Owing, however, to the popular outcry against arsenic in any form, its use is now almost entirely restricted to the production of lithographic colours; whereas, formerly, vast quantities were used by paper-stainers who have now gone to the other extreme, and demand that colours supplied to them shall be guaranteed free from arsenic.

The value of a commercial sample of white arsenic depends upon the amount of As_2O_3 which it contains, and for general purposes this is the only estimation that is required. In order to ascertain this amount, we must first make a standard iodine solution, and to obtain this we proceed as follows: Weigh out carefully 12·7 grammes of pure resublimed iodine, and 18 grammes of pure potassium iodide, and dissolve these together in cold distilled water, and make up the solution to 1000 cc. The strength of this solution must be accurately ascertained, and to do this we weigh out exactly 4·95 grammes of perfectly pure resublimed arsenious acid, and 25 grammes of pure sodium carbonate, and dissolve the two substances by boiling with about 500 cc. of water. The solution is accelerated by constant stirring, and when complete the liquid is allowed to cool, and afterwards made up to 1000 cc. From this latter solution we measure out, preferably by means of a burette, 10 cc., and place the same in a white porcelain basin. This liquid is diluted with cold distilled water to obtain a suitable bulk for working with, and a few drops of a weak solution of starch in distilled water are then stirred into the contents of the basin. A burette is now filled with the iodine solution, which is allowed to run drop by drop into the basin, stirring the whole constantly until a faint but permanent blue colour is visible. This indicates the end of the reaction, and assuming that 10 cc. of the iodine solution have been used, its strength expressed in the equivalent of As_2O_3 is such that 100 cc. = 0·495 gramme.

Having by this method accurately estimated the strength of the iodine solution, we proceed to the examination of the sample as follows: Weigh out accurately 2 grammes, and dissolve the same by boiling in distilled water containing about 5 grammes of pure sodium carbonate. When cold, the solution is made up to 500 cc., and of this made-up solution 100 cc. (which represents 0·4 gramme of the original sample) are withdrawn for analysis, and placed in a white porcelain basin. A few drops of the weak starch solution are added, and the whole is titrated with the standard iodine solution, in the manner already described, until the faint but permanent blue colour is noticed. Then from the number of cc. of the standard solution so required, we can readily calculate the amount of As_2O_3 present in the sample. Thus assuming that the 100 cc. required 80 cc. of the standard iodine solution, the 2 grammes of the sample originally taken would require 400 cc., and consequently 100 grammes would require 20,000 cc. As 100 cc. of the iodine solution are equal to 0·495 gramme, As_2O_3, 20,000 cc. = 99 grammes of that substance, which is the percentage contained in the sample under examination.

Formerly several arsenical green colours were largely used by paint manufacturers, and large quantities of such were sold in both the pulp and dry condition to paper-stainers, but owing to the public outcry against arsenical colours, the use of such pigments has been greatly retarded, and now they are used only for lithographic or letter-press work. Of these colours by far the most important is emerald green, which consists largely of an aceto-arsenite of copper, and when pure it presents a peculiar and characteristic bluish-green tint, which possesses a brilliancy and depth of tone that up to the present has not been equalled upon a less objectionable base.

Samples of this green should be carefully examined for purity of tone, covering power, and freedom from grit, by the usual tests. If pure, it should dissolve completely in hydrochloric acid, and the solution so obtained should be tested by barium chloride, which will show, by the formation of a white precipitate, the presence of a sulphate as an impurity, and if such is detected it will probably indicate the presence of gypsum. Should any residue remain after boiling with hydrochloric acid, it must be tested, and will probably prove to be barytes. Any effervescence on the addition of hydrochloric acid will indicate the presence of a carbonate, probably chalk.

Emerald green cannot be used in conjunction with any other colours or bases which contain sulphur, as owing to the presence of copper in the green the mixture gradually becomes darker in tone, owing to the formation of copper sulphide, which is a black-coloured substance. It can be used, however, with many bases; and, it is possible, that for the purposes enumerated, it will hold the field successfully against rival colours in spite of its objectionable nature.

Owing to the demands of paper-stainers for pulp and dry colours which are free from arsenic, the following very delicate tests are given for its detection when present in very minute quantities. The first of these, known as Reinsch's test, consists in boiling the suspected sample with dilute pure hydrochloric acid, along with a piece of bright copper foil, in a test-tube. When arsenic is present even in minute quantities, an iron-grey film of metallic arsenic will be deposited upon the bright surface of the copper; and, if a large amount of arsenic is present, the film so obtained will increase in thickness, until it peels off the copper in the form of thin black scales. The alternative and more delicate method is known as Marsh's test, and by means of it the operator is enabled to detect exceedingly minute traces of arsenic.

The apparatus required in order to conduct this test consists of a glass flask fitted with a tight-fitting india-rubber cork, bored in two places, through one of the holes in which is introduced a safety funnel, and through the other an ordinary calcium chloride drying tube is inserted. The outer end of this tube is joined on to a piece of hard glass tube by means of a tight-fitting piece of india-rubber tubing. The glass tube is first of all drawn out in the blowpipe flame until it prevents the appearance of about three inches of its length being of the ordinary diameter, this portion being joined on to another length of about one inch (of the ordinary diameter) by means of a very fine drawn out connection, the whole terminating in a long and finely drawn out tube. Thus the tube now consists of four parts, two of which are of the original diameter, the other two portions being drawn out as finely as possible, without entirely closing the tube.

Hydrogen gas is now evolved in the flask by means of redistilled zinc and pure dilute sulphuric acid, and this passes along through the calcium chloride, by which the moisture is absorbed, until it emerges from the second of the finely drawn portions of the glass tube. The gas must be evolved briskly, and after several minutes have elapsed in which the air originally contained in the apparatus is driven out, a light may be applied to the hydrogen as it emerges from the tube, but great care must be taken in so doing, as unless all the air has been expelled an explosion will ensue, which will certainly wreck the apparatus. Assuming that a light has been successfully applied to the hydrogen as it emerges from the tube, a Bunsen burner is placed under the long length of the glass tube, close to the point where it tapers off, into the narrower portion and the shorter length beyond the first narrow connection is carefully watched. Should a faint brown coloration be there noticed, it will indicate the presence of arsenic in one or other of the reagents employed, and if such is the case they must be rejected, and others used until both zinc and acid are found free from arsenic. When this is the case, the sample under examination is thinned down with water, and added to the flask by means of the safety funnel. Should a faint brown coloration or grey mirror be observed upon the tube, it will indicate the presence of arsenic or antimony in the sample. The same result can be obtained by neglecting the use of the middle portion of the tube and by holding a piece of cold white porcelain such as a crucible lid in the hydrogen flame, when if arsenic be present either in the reagents or sample, a brown or black stain will appear upon the white porcelain.

The process described above depends upon the liberation of arseniuretted hydrogen within the flask in the first case, and as this passes along and through the apparatus, it is decomposed by the heat of the Bunsen flame into its elements arsenic and hydrogen. The former condenses on the cool portions of the glass tube, where it is easily seen and recognised.

ANTIMONY COMPOUNDS.

The only compound under this heading which finds an extensive use in the colour works is tartar emetic, which consists of a double tartrate of antimony and potassium having the lengthy formula $(SbO)\ KC_4H_4O_6 + \frac{1}{2}\ H_2O$, and when pure it contains 43·4 per cent. of Sb_2O_3, commercial samples being sold with a guarantee that the product contains 43 per cent. of Sb_2O_3. In practice it is used along with tannic acid to precipitate the basic coal-tar colours in the manufacture of lakes, and so finds an extended use, but if the ultimate colour is intended for the use of paper-stainers, the use of this salt cannot be recommended, for the presence of antimony is looked upon by the trade with as much suspicion as that of its near relative arsenic, and indeed the first test to which such colours are subjected will indicate the presence of antimony as well as arsenic.

The value of all samples is judged by the percentage of Sb_2O_3 they contain, and this is estimated in the following manner: Weigh out carefully 25 grammes of the sample, dissolve in hot distilled water, and make up to 500 cc. in a standard flask. For the analysis measure out, preferably by means of a burette, 50 cc. of this made-up solution, and place the same in a white porcelain basin, and neutralise exactly with a solution of pure sodium carbonate. Then add 20 cc. of a saturated solution of sodium bi-carbonate ($NaHCO_3$), and titrate with the standard iodine solution described under arsenic compounds. As the end of the reaction approaches, it will be indicated by the increasing slowness of the decoloration of the iodine within the basin, and at this point a few drops of a weak starch solution are added, and the titration is continued until a faint but permanent blue coloration remains. The reaction is then complete, and as 100 cc. of the standard iodine solution = 0·72 gramme Sb_2O_3, we can readily calculate the strength of the sample under examination.

CALCIUM COMPOUNDS.

Under this classification there are several substances in constant use both in the paint and colour mixing departments of the average works. The most important of these are the oxide CaO, also known as quick-lime or burnt lime; the hydroxide $Ca(OH)_2$, better known as calcium hydrate or slacked lime; the sulphate, known as gypsum, which has the formula $CaSO_4 + 2 H_2O$; the chloride $CaCl_2$; and the carbonate $CaCO_3$, which is also known as chalk or whiting. Of these the oxide, hydroxide and chloride are less used than the others, but all are important, and the carbonate and sulphate frequently enter largely into the composition of paints and bases for lakes.

The value of each is best judged by a consideration of the use to which it will be put, and it will be at once evident that we need not insist upon such a high degree of purity when the product is intended for use in dark paint mixtures, as when it is required for a brilliant lake.

When the oxide, hydroxide and chloride are intended for use in connection with Madder Reds, it will be necessary to see that the products are perfectly free from iron, and this can be readily ascertained by dissolving the sample in pure hydrochloric acid, and testing in the manner already described under the aluminium compounds. The carbonate and sulphate appear in commerce in many degrees of shade, purity and price, and in judging the respective values of samples the operator must largely depend upon his own judgment, but as a general rule all samples should be judged by the amount of oxide (CaO) which they contain, and this is estimated in the following manner:—

Weigh out 5 grammes of the sample, and dissolve in dilute pure hydrochloric acid at the boil. Any insoluble matter which remains can be filtered on to a Swedish filter-paper, which is well washed with hot distilled water until free from acid, the washings and original solution being afterwards made up to 500 cc., and the residue dried and estimated in the usual way. For the purpose of the analysis, measure out 100 cc. of the made-up solution, which is equal to 1 gramme of the original sample, and after placing in a beaker, dilute slightly with water and raise to the boil. About 25 cc. of a saturated solution of ammonium chloride are now added, and the whole rendered alkaline with ammonium hydrate, and the boiling continued for a few minutes. Should any flocculent precipitate of aluminium hydrate be noticed, it can be filtered off and estimated in the manner described under aluminium compounds, and the filtrate and washings are next examined for calcium compounds. This is done by again boiling the liquid, adding a few drops of ammonium hydrate, and about 25 cc. of a saturated solution of ammonium oxalate, when a white precipitate of calcium oxalate will be observed. The boiling is continued for about ten minutes, the liquid and precipitate being then filtered through a Swedish filter-paper. The precipitate is well washed with hot distilled water until free from soluble salts, and is then put to dry in the air-bath, and afterwards ignited in the manner described for the estimation of calcium salts in the consideration of zinc compounds, the same factors as there given being used in the subsequent calculation. The filtrate and washings are then treated in exactly the same manner as described for the detection of magnesium compounds in zinc compounds, and it will be noticed that the analysis of calcium compounds is conducted generally as described already under zinc compounds, the same impurities being common to both.

In storing calcium compounds in the works, it may be observed that it is requisite to keep the oxide and chloride well covered up and away from atmospheric influences, as both substances are strongly deliquescent and absorb moisture very readily.

BARIUM COMPOUNDS.

Under this heading we meet with two substances which find a very extensive use in the colour works, one of these being the chloride $BaCl_2 + 2\,H_2O$, very soluble in water, and the other being the sulphate $BaSO_4$, better known as barytes, which is quite insoluble. The former is largely used as a precipitating agent in the preparation of lakes from what is known as the acid series of coal-tar colours, and also in the manufacture of Satin and Enamel whites, and the latter is largely used as a base or body for many colours, and also for the preparation of paints, in which it is used to a very considerable extent, although as regards covering power it ranks inferior to white lead, but is slightly superior to zinc white.

The chief impurity found in barium chloride is iron; although, if due care has been observed during the manufacture, even the last traces of this impurity should be eliminated. The test for iron is made exactly as described under the aluminium compounds, and as in some cases it becomes necessary to estimate the amount of barium present in a sample, the following process is recommended :—

Weigh out accurately 10 grammes of the sample, dissolve in warm distilled water, and make the solution up to 1000 cc. From this made-up solution take out 100 cc. (equal to 1 gramme of the original sample) for the purpose of the analysis, and after placing the same in a beaker, dilute with distilled water, and raise the whole to the boil. When this point is reached, add slowly sufficient dilute pure sulphuric acid to precipitate all the barium present as sulphate, and continue the boiling for about ten minutes, as by so doing the precipitate assumes a form in which it is easier to filter. Then set aside the beaker, and allow the precipitate to settle, which it does with rapidity owing to its weight. When the precipitate has settled, it can be washed several times by decantation, until the clear liquid is free from acid, and it is then collected upon a Swedish filter-paper, dried, and ignited in the usual manner in a tared platinum crucible, and after deducting the weight of the crucible + filter-paper ash from the total weight obtained, we have the amount of $BaSO_4$ yielded by 1 gramme of the sample, and for the purpose of assisting the calculation it may be stated that 233 parts of $BaSO_4$ correspond to 153 parts of barium oxide BaO, or to 244 parts of crystallised barium chloride $BaCl_2 + 2\ H_2O$. A good sample of commercial crystals will show about 99 per cent. of $BaCl_2 + 2H_2O$, when calculated as above, and should the sample fall much below that figure, it should be rejected, as there are several brands now upon the market which yield that result with regularity.

Barytes, owing to its insolubility, cannot be treated as above, and an analysis of it for the percentage of barium sulphate is rarely required; as, owing to the cheapness of this product, it cannot readily be adulterated—any substances which might be used for that purpose costing as much or more than the compound under notice. As a preliminary investigation it should be examined for its purity of shade, as all tones from pure white to silver grey are found, and another desirable quality is freedom from grit, and here again various brands give varying results. The presence of iron can be detected by boiling a few grammes of the sample with pure dilute hydrochloric acid, dividing the liquid into two equal portions, and testing as described under the aluminium compounds. The amount of iron present is usually so small that it may be neglected, although the judgment of the observer must decide upon the point, as he will know for what purposes the sample is intended. The comparative covering powers of the various samples must also be noticed, and if all other essentials are equal, the sample giving the best result in this connection should be selected. It may here be pointed out that the degree of fineness which a sample possesses over one previously in use should be carefully noticed, for in many colours such as Brunswick-greens, blues and vermilionettes, the addition of finer barytes than usual will make the ultimate shade appear weaker, and in the case of a coarser barytes the sample will appear stronger.

When it is desired to estimate the percentage of $BaSO_4$ in a sample of barytes, the following method can be adopted, although as already stated such a proceeding is unusual: Weigh out carefully 2 grammes of the sample, and mix the same thoroughly with about 10 grammes of a mixture of powdered carbonates of soda and potash in equal proportions. This is done in a mortar, and care must be exercised to make an intimate mixture. The contents of the mortar are then transferred to a platinum capsule, carefully brushing by means of a feather the last traces of solid matter from the mortar into the capsule, the contents of which are then fused over a blowpipe flame until the whole mass is in a state of perfect fusion. If the fusion does not become complete, and white particles of undecomposed barytes are seen floating about in the clear fused liquid, more of the mixture of the carbonates must be added until the fusion is complete. When this is accomplished, the capsule and its contents are set aside to cool, and then placed in a deep beaker which is covered with a clock-glass. Pure dilute hydrochloric acid is then added until effervescence ceases, the under side of the clock-glass is carefully rinsed with distilled water, the capsule is raised and thoroughly washed with distilled water, and the contents of the beaker are transferred to a standard flask, and the solution made up to 500 cc. As we have now a solution of barium chloride, the rest of the analysis is carried out exactly as described for that substance, and if we take from the made-up solution 250 cc. for the analysis, we shall then be working on the equivalent of 1 gramme of the original sample. In the subsequent calculation of results, the factors already given are used, and it may be stated as a guide that a good sample of barytes should not yield less than 99 per cent. of $BaSO_4$.

CADMIUM COMPOUNDS.

Owing to the high price of these compounds, they are exclusively used in the higher branches of the tinctorial arts; and considering the great brilliance and permanency of the various yellow shades which they embrace, it is greatly to be regretted that they cannot compete on more favourable terms with other and inferior substances. Practically all shades of cadmium yellow are due to various processes employed in preparing the sulphide, which has a chemical composition represented by the formula CdS, and this compound is the most noticeable of all those obtained from metallic cadmium, especially from the point of view of those engaged in the colour trade, as most of the other compounds are colourless.

Cadmium yellow may be adulterated with other yellow sulphides such as those yielded by tin, arsenic and antimony, but it is to the credit of manufacturers that any such additions are but rarely detected in commercial samples. The presence of such adulterants is readily perceived by warming the sample with ammonium sulphide, in which reagent the three sulphides mentioned above are soluble, but in which cadmium sulphide is insoluble. After filtering the liquid, the clear filtrate is treated with an excess of pure hydrochloric acid which will precipitate the sulphides of tin, arsenic or antimony, and so indicate adulteration.

In dealing with an expensive article such as cadmium yellow, it is always advisable to submit it to careful analysis; and in this case it would be necessary to estimate the percentage of metallic cadmium contained in the sample, and to express that result in terms of CdS. To do this we can adopt two methods, one of which depends upon the precipitation of cadmium as carbonate, and the other upon its precipitation as sulphide, the following being the processes to be followed:—

Weigh out 1 gramme of the sample, and boil it in pure hydrochloric acid, in which reagent it should dissolve completely, unless contaminated with some impurity. When the solution is complete, and whilst the liquid is still boiling, a saturated solution of pure sodium carbonate is added until all the acid is neutralised, and the cadmium precipitated as carbonate. As the normal carbonate of cadmium is not known, the formula of the above precipitate cannot be given, as it is said to vary with the temperature and amount of alkali used. During the operation just described, the beaker must be covered with a glass to prevent loss from the violent effervescence which takes place, and at the end of the operation the under side of the glass is well washed with distilled water, which is allowed to run into the beaker. The contents of the beaker are then filtered through a Swedish filter-paper, upon which the precipitate is well washed with hot distilled water, until the washings are free from alkali. The filter and its contents are then dried in the air-bath at about 105° C., and afterwards ignited in the usual manner in a porcelain crucible. This converts the carbonate into the oxide CdO, and 128 parts of this compound correspond to 112 parts of metallic cadmium, or to 144 parts of CdS.

The alternative process to the above consists in dissolving the same weight of the sample in a similar manner to that already described, diluting the solution somewhat with distilled water, and allowing a stream of sulphuretted hydrogen gas to bubble briskly through the liquid for about fifteen minutes. This precipitates the cadmium as the sulphide, and the precipitate is carefully filtered on to a Swedish filter-paper which has been previously thoroughly dried and weighed. The contents of the filter are washed perfectly free from acid by means of hot distilled water, and the whole is then dried in a water-bath and weighed, the increase in weight between the first and second weighings giving the amount of CdS contained in 1 gramme of the sample.

MERCURY COMPOUNDS.

There is only one substance to be considered under this heading, that being the well-known vermilion, which is a compound of metallic mercury and sulphur, having a chemical composition represented by the formula HgS, in which 200 parts by weight of mercury are combined with 32 parts of sulphur. This compound has long been known as a valuable pigment, on account of its characteristic scarlet colour, and the excellent covering properties which it possesses, together with its permanent qualities when used as an oil colour.

Owing to the high price of mercury compounds generally, this substance may be adulterated with any other bright red pigment such as oxide of iron, red or orange lead, or even by the addition of any of the precipitated eosin lakes which are known in the trade as vermilionettes. Fortunately any such addition can be readily detected by a very simple test, which is conducted as follows: Weigh out 2 grammes of the sample, placing the same in a tared porcelain crucible, and heat gently over a Bunsen flame until the whole of the vermilion has burned away, taking care not to inhale the vapours which arise, and to allow the air to have free access to the contents of the crucible. When the ignition is complete, the crucible is weighed, and if the sample was pure, the amount of residue which remains should not exceed 0·5 per cent. If this figure is exceeded, the residue should be examined for any or all of the likely impurities enumerated, the tests for which have already been described under their various compounds. If the presence of vermilionette is suspected, a small quantity of the sample is boiled with alcohol and sodium carbonate in a test tube, when the presence of eosin and consequently vermilionette is recognised by the characteristic fluorescence which those colours always produce under such treatment.

ULTRAMARINE.

This valuable blue colour which is largely used both in the paint and colour departments varies greatly in shade, and also in composition, the differences being due to details in the manufacture which are explained fully in all works of reference. For its production various mixtures of china clay, sodium carbonate, sodium sulphate, sulphur and carbon are employed, and it is easy to perceive that by varying the proportions used, substances of varying composition will be produced. Therefore, owing to the complicated nature of all ultramarines, no reliable process of chemical analysis can be laid down as a guide to the purity of any sample, and it is usually only requisite to compare competing samples for colour, covering power, and freedom from grit. The former test is generally performed by letting down equal weights of the samples, with a definite amount of zinc white, using linseed oil as the mixing medium, and finally comparing the strength of colour as then shown. Should price and other essentials be equal, the sample which exhibits the greatest depth of tone after so diluting or letting down is the one naturally selected.

Should it be desired for a particular purpose to submit the sample to a more exhaustive test, the principal ingredients can be separately estimated, although it must be admitted that results so obtained do not furnish very reliable indications. The principal ingredients are moisture, alumina, silica and sulphur, and these can be estimated in the manner herein described.

The moisture is estimated by heating about 2 grammes on a tared watch-glass for about four hours, at a temperature of about 110° C., in an air-bath. When the sample ceases to lose weight, the difference between the original and final weights will indicate the amount of moisture contained in the weight of the sample under examination, and these figures should be calculated to, and expressed in, percentage.

The silica present is estimated by heating about 2 grammes in a beaker with pure hydrochloric acid until the original blue colour is completely destroyed. The contents of the beaker are then transferred to a porcelain basin and evaporated to complete dryness, which is accelerated by frequent stirring with a glass rod. The dry residue is then more strongly heated for a few minutes over the Bunsen flame, and after cooling it is treated with pure hydrochloric acid and warmed slightly. The insoluble matter which remains after this treatment is silica, and it is carefully filtered on to a Swedish filter-paper, where it is well washed with hot distilled water until perfectly free from acid. The filter paper and its contents are then dried in the air-bath, and afterwards ignited in a tared platinum crucible, the increase in weight showing the amount of SiO_2 yielded by the quantity of the sample taken for analysis, which result must be calculated to, and expressed in, percentage.

The filtrate and washings from the last operation must be carefully preserved, and are tested for the amount of alumina (Al_2O_3) which they contain. This is done by precipitation with ammonium hydrate in the manner already described under aluminium compounds. The result is expressed in percentage of Al_2O_3.

To estimate the total sulphur present, which may exist both as free sulphur and sulphates, it is necessary to weigh out about 2 grammes of the sample and heat the same in a beaker with a mixture of 2 parts of pure nitric acid, and 1 part of hydrochloric acid. When the original colour of the sample has been destroyed, the boiling is continued for fifteen minutes to oxidise the free sulphur and the liquid is cooled and filtered. The residue which remains upon the filter is silica, and the filtrate contains the sulphur, as sulphuric acid or sulphates which is then precipitated by the addition of a cold saturated solution of barium chloride. The filtrate should be raised to the boil before the barium chloride is added, the boiling being continued for some time after complete precipitation is effected, as by so doing the precipitate assumes a more granular form, and is easier to filter. When all the precipitate has settled, it is filtered on to a Swedish filter-paper, where it is washed with hot distilled water until free from acid, which is indicated by blue litmus paper ceasing to turn red. The filter is then dried in the air-bath, and ignited in the usual manner in a tared platinum crucible, the result showing the amount of barium sulphate ($BaSO_4$) contained in the quantity of the sample under examination. The result so obtained should be calculated to express the percentage of sulphur in the sample, and as a guide it may be stated that every 233 parts of $BaSO_4$ correspond to 32 parts of sulphur (S). The next step is to distinguish between the sulphur which exists in the free state and that which is combined as sulphates, and to do this the process first described is followed in detail, except that the use of nitric acid is omitted. The result will show the amount of sulphur existing as sulphates and it can be expressed in terms of sulphur trioxide (SO_3) which is the oxide corresponding to sulphuric acid. The amount of actual sulphur ascertained by this test is subtracted from the total previously found, and we thus obtain two results, one showing the percentage of free sulphur in the sample, and the other the amount of sulphur existing as SO_3.

As a guide to the interpretation of the results so obtained, the detailed compositions of different brands of ultramarine are set forth in many of the standard works upon the subject, but the average chemist usually places more reliance upon the simple mechanical tests first alluded to than upon those obtained by an exhaustive chemical analysis.

COBALT COMPOUNDS.

Under this classification there are two substances worthy of notice, both possessing a blue colour. They are known respectively as Smalt, which consists of a cobalt silicate ; and cobalt blue or cobalt ultramarine, which is a compound of cobalt oxide and alumina, with or without phosphoric acid. The former compound, which is in reality a potash glass coloured with cobalt oxide, has now been almost entirely replaced by the more effective ultramarine blue, and its use is extremely limited. The latter compound occupies a high place in the estimation of artists, owing to its pure tint and general permanence.

It is rarely that an analysis of this compound is required, and it will be sufficient for ordinary purposes if the purity of shade possessed by competing samples is tested comparatively—either in the dry state, or after letting down with a definite quantity of zinc white.

CARBON COMPOUNDS.

Under this heading we have to consider an important class of black-coloured substances, which play a useful and extensive part in both branches of the colour works. Speaking generally it may be affirmed that all the black pigments of commerce owe their colour, either wholly or in part, to the presence of carbon. Such carbon blacks are sold under a variety of names, some indicating the source of origin, others being more or less fancy trade terms. Thus we encounter lamp black, carbon black, pure black, wood or vegetable black, mineral black, bone black, ivory black, animal black, drop black, Frankfort black, etc.

All these various substances can be divided into three classes—mineral, vegetable and animal. Under the former classification are included coal and coke, substances of but little value to the paint or colour manufacturer, but which enter into the composition of certain of the black paints now found upon the market; but another series of useful blacks obtained from the same source and known as carbon blacks, are obtained by burning natural gas and the otherwise useless residue obtained during the refining of petroleum. The vegetable series includes all blacks obtained from charcoal or vegetable oils, and those of the animal series are obtained by the calcination of bones or animal matter.

All these blacks possess similar properties, but vary considerably in intensity of shade, fineness, and covering power, for all of which they should be tested, and the comparative results carefully observed.

As the amount of carbon present is the essential by which the value of a sample is usually judged, the following simple process for its estimation can be followed. Weigh out in a tared platinum capsule about 3 grammes of the sample, and heat over an ordinary Bunsen gas-flame until all the carbon has burned away and nothing remains but a white or grey-coloured ash. This operation may take a considerable time for some varieties of carbon—particularly graphite—do not readily ignite, and when the ignition is complete, the capsule is cooled and weighed, and the increase in weight will show the amount of mineral matter or residue contained in the sample. The loss in weight indicates both the amount of carbon and moisture present, and in order to separate this result into its two factors it will be necessary to estimate the amount of moisture, as follows: Weigh out, on a tared watch-glass, about 5 grammes of the sample, and place in the air-bath (which may be heated up to 110° C.) for about six hours. When no further loss of weight is noticed the glass with its contents is finally weighed, the total loss in weight representing the amount of moisture present. This result must be subtracted from the total loss in weight on the ignition already described, the balance being put down as carbon. Thus we have three results showing the amount of carbon, moisture and mineral residue, and for all practical purposes they are quite sufficient. The following analyses of various blacks will indicate the average percentage composition of such substances, and will serve as a useful table for reference:—

	Mineral Oil Carbon Black.	Coke.	Beech Charcoal.	Bone Black.
Carbon . . .	97·25	93·37	89·75	16·12
Moisture . . .	1·62	0·43	7·23	7·04
Residue . . .	1·05	6·20	3·02	76·84

Should it be desired to ascertain rapidly whether a sample is of animal or other origin, the following test is applied, and it depends for its adaptation on the fact that all bone blacks contain quantities of calcium phosphate and carbonate as an essential part of their composition, the amount being frequently as high as 75 per cent. To detect the presence of these calcium salts which indicate the animal origin of the sample, a few grammes are ignited as already described, the resulting residue being then boiled in hydrochloric acid and afterwards filtered. To the cooled filtrate an excess of ammonium hydrate is then added, when a bulky white precipitate indicating phosphate of lime will be obtained. When further additions of the reagent produce no further precipitate the liquid is filtered, and to the filtrate a few cc. of ammonium oxalate are added, and the whole is well boiled. A white precipitate of oxalate of lime will be observed, and these two results taken together will indicate a bone black, for charcoal and other vegetable blacks contain no phosphates, although they may contain a small amount of calcium salts.

As there are many blacks now upon the market which consist of a mixture of carbon black with a dark-coloured aniline lake, the following simple test will serve to distinguish between such a mixture and a black entirely composed of carbon, the test depending upon the well-known insoluble character of the latter element. Two separate portions of the sample are boiled in a test tube with dilute solutions of acetic acid and carbonate of soda respectively, and the liquids are afterwards filtered. If the solutions are coloured, they will indicate the presence and nature of a coal-tar colour, as the former solution will contain any such basic colouring matter, and the latter will be coloured by one or other of the acid series of dye-stuffs. Should no coloration be apparent, the sample can be safely put down as being a carbon black.

The only other black pigment which finds an extended use in the colour trade is the black oxide of manganese, which differs from all carbon blacks in being soluble in hydrochloric acid, and which has already been considered under the manganese compounds.

OILS.

Under this heading we have to deal with the examination of two substances—oleïn, or turkey red oil, and linseed oil. The former is largely used by the colour-maker to precipitate the basic coal-tar colours in the manufacture of lakes, and the latter in one form or another enters into the composition of all paints.

Oleïn is a name applied to various products which differ but slightly from each other, all being obtained by the action of sulphuric acid upon a vegetable oil at the ordinary temperature, with subsequent neutralisation by means of caustic soda. The oil usually employed is castor oil, and the finished product has the property of mixing with water in all proportions. It is found in commerce as a thick brown oily-looking liquid, which yields on analysis from 20 to 60 per cent. of fatty acids, according to the brand or quality.

Linseed oil is obtained by crushing and extracting the seeds of the flax plant, and its manufacture forms a large industry. It comes upon the market in various degrees of quality, such being known as "raw," "boiled" and "refined," the two latter being prepared by various processes from the former.

As samples of oleïn are judged for value by the amount of fatty acids which they contain, the following process for the estimation of the same can be followed:—

Weigh out 10 grammes of the sample into a beaker having a capacity of about 500 cc., and half-fill the same with distilled water. This is then heated over a Bunsen flame, and whilst this operation is proceeding an excess of hydrochloric acid is stirred in. The contents of the beaker are heated almost up to the boil with constant stirring, and 10 grammes of white wax are carefully weighed out, and then stirred into the beaker. When all the wax has melted, the whole is again well stirred, and the beaker is then set aside to cool. When this is accomplished, and the wax has set hard upon the surface of the liquid, the cake which contains the fatty acids plus the amount of wax added, is transferred to a small tared beaker, great care being taken to detach any pieces of wax which may still adhere to the sides of the first beaker, and to add such to the contents of the second beaker, which is then heated slowly and carefully over an Argand burner with more distilled water, to wash the cake of fatty acids and wax. This beaker is heated until the cake is entirely melted, when it is set aside and allowed to cool. When the cake has again become hard, the water underneath is poured away, taking care that no loose pieces of wax flow along with it, and finally the cake is again heated until liquid, over the Argand burner, and the liquid mass is continually stirred with a glass rod of known weight, until no globules of water are seen floating in the liquid. The beaker is again allowed to cool, and then weighed, and by deducting from the total weight the combined weights of the beaker, glass rod, and wax added, we obtain the amount of fatty acids yielded by 10 grammes of the sample, the result so obtained being then calculated to percentage.

Samples of linseed oil should be examined for adulteration with cheaper and inferior oils, those usually found in this connection being resin and mineral oils. The specific gravity is usually a good index as to the character of linseed oil, and any adulteration it may contain, as that of a good sample of linseed oil should stand between 0·927 and 0·936, and if lower than the former, the presence of mineral oil may be suspected, and if higher than the latter, resin oil will probably be detected by subsequent tests. Boiled linseed oil should show a specific gravity varying between 0·940 and 0·950, and the same adulterations may be suspected if the sample registers below or above these figures.

The flash-point, or degree of temperature at which a sample takes fire when heated in a suitable apparatus affords another useful test of the purity of the sample, as it confirms any suspicions raised by the specific gravity. There are several forms of apparatus sold by dealers in laboratory requisites, for conducting this test, all of which rely upon the indication by means of a thermometer, of the degree of heat at which the sample ignites. Linseed oil should flash at about 225·5° C., and as the flashing point of both mineral and resin oils is below that of pure linseed oil, a sample which ignited several degrees earlier should be regarded with considerable suspicion; and, if any resin oil is present, the characteristic odour of burnt resins will be easily detected during the process, and especially when the temperature rises above 133° C.

To determine more accurately the presence of such adulterants in either "raw" or "boiled" linseed oil, weigh out about 25 grammes into a small flask, and boil with an alcoholic solution of caustic soda. This operation saponifies the linseed oil, and after the whole has been boiling for about an hour, the contents of the flask are cooled, and then transferred to a separating funnel, to which more water and some ether is added, and the whole is shaken vigorously for about three minutes. The funnel is then set aside until its contents have separated into two distinct layers, the upper one of which will consist of the ether plus any mineral or resin oil contained in the original sample. The lower liquid is run off, and the ether is washed several times with water, the funnel being allowed to stand after each operation until its contents have separated into the two layers, the bottom one being run off as described. Finally the ether is run into a tared flask, from which it is evaporated off over a water-bath; and, when all is evaporated, it is still necessary to dry the contents of the flask more thoroughly to get rid of the last traces of moisture, and this is accomplished by heating cautiously over a Bunsen flame, and blowing cold air into the flask. When the contents of the flask are thoroughly dry, it is cooled and weighed, the increase in weight indicating the amount of impurity present in the quantity of oil examined. The nature of the residue will indicate whether mineral or resin oil is the impurity; if the former it will be light in nature and colour, and if the latter it will be heavy, and dark in colour; and this can be further confirmed by heating the contents of the flask strongly, when, if resin oil is present, the characteristic odour will be at once perceived.

To detect the presence of driers and their nature in boiled oil, it is necessary to boil about 50 grammes of the sample for about an hour with pure dilute hydrochloric acid, and then to filter the liquid so obtained. The clear filtrate will then contain any lead, manganese, zinc or iron salts, which have been used as driers, and these can be tested for by the several methods given in the consideration of their various compounds.

In conclusion, it may be added that many of the tests given in the foregoing article may be altered or modified to suit the particular requirements of the sample under examination, and at times it may also be necessary to add certain others which may appeal to the operator, but taking those given as they stand, they will serve as a useful guide in the majority of cases, and it is hoped that the simplified examples of the necessary calculations will prove a useful addition to the usual stock of laboratory literature.

Although the articles enumerated as raw materials do not by any means exhaust the usual stock found in any paint or colour works, it will be seen that they embrace the more important products in each division, and when the examination of any substances not enumerated in this list is called for, such can be undertaken by some of the tests given, and in order to do this it will simply be necessary to ascertain what particular ingredient is to be estimated, and then to study the methods set forth in the consideration of one or other of the various classes of compounds.

Familiarity with the methods given will enable the operator to get through a large amount of work, and the successful chemist is the one who, having studied the various processes, has selected the one most fitting to his requirements, and by a judicious arrangement of time and materials will arrange to have several samples under examination at one and the same time, and whilst one is filtering or cooling, another is put in hand. This is always advisable, for results so obtained have the great merit of being comparative, which after all is the ultimate object to be attained by any methods of chemical analysis.

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