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DETERMINATION OF ACIDIC GROUPS IN COAL TARS BY NON-AQUEOUS TITRATION

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Determination of Acidic Groups in Coal Tars by Non-aqueous Titration

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ABSTRACT

The acidic groups in tars obtained by low-temperature carbonization of a high-volatile C bituminous coal at different temperatures up to 600°C were determined by titration with sodium aminoethoxide in ethylenediamine. All the titration curves showed three inflections, but it was thought that the first two were caused by groups of the same general acidic strength. Apart from the small yield of tar of low acidity obtained at 350°C, the acidity was found to decrease from 5.66 milliequivalents per gram at 400°C to 4.64 milliequivalents per gram at 500°C and then increase again to 5.74 milliequivalents per gram at 600°C. The component acidities followed the same trend, and the ratio of strongly acid groups to weakly acid groups increased with increase in the carbonization temperature.

INTRODUCTION

The usual methods of determining tar acids by extraction with aqueous alkali are time consuming and may not detect weakly acidic groups. In contrast, titration in a non-aqueous basic medium is often used as a convenient method for determining such groups. This was demonstrated for coal hydrogenation oils by Katz and Glenn (1952), who applied a standard extraction procedure and determined the distribution of acidic groups in extracts and residues.

While working with J. D. Brooks (1956) on a study of ion-exchange chromatography of coal tar and pitch, I used the non-aqueous titration method to determine the acidity of the fractions obtained from a pitch by both ion-exchange and extraction methods. Non-aqueous titration has been applied in the present investigation to determine acidic groups in tars obtained by the carbonization of a coal at different temperatures up to 600°C.

The tars examined in this study were obtained as by-products in the course of an investigation of variation of acidic groups in fresh and oxidized coals during carbonization (Maher, Harris, and Yohe, 1959).

COAL USED

The coal used was a fresh specimen of high-volatile C bituminous coal from a strip mine in the No. 6 seam in Knox County, Illinois. There was about 50 feet of overburden at the site of sampling.

The coal was taken as a block that weighed about 10 pounds and was brought to the laboratory in a sealed can. The outer portions were chipped off to leave a five-pound center core that was put through a jaw crusher and left overnight in a

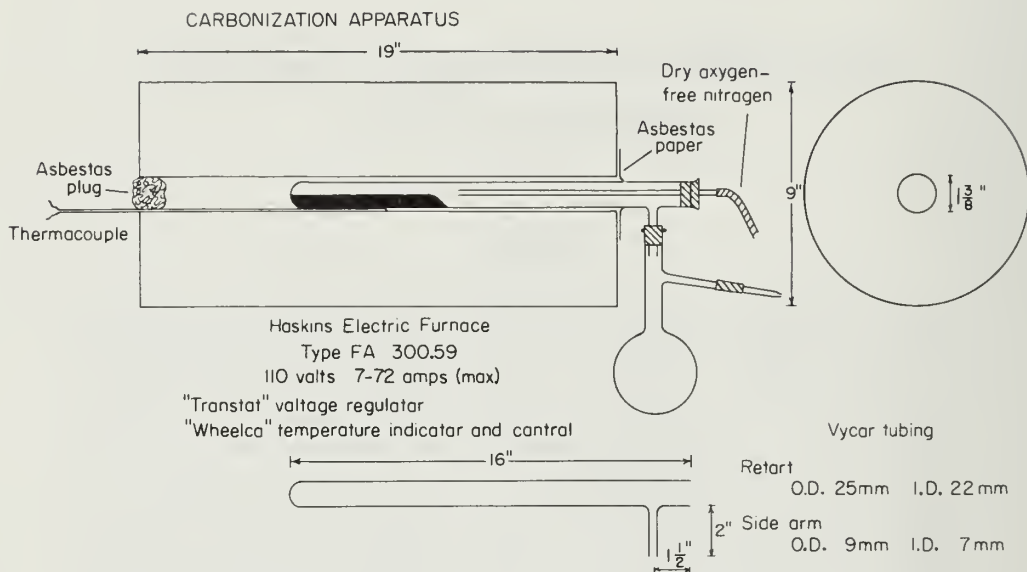


Fig. 1. - Carbonization apparatus.

nitrogen-filled desiccator over calcium chloride, then further crushed in a roll mill, and finally reduced to minus 60-mesh in a nitrogen-filled ball mill. It then was thoroughly mixed and stored in small bottles, each of which held enough coal for two carbonization charges.

Exposure of the coal to air was kept to a minimum, and all containers were flushed out with nitrogen before the coal was introduced.

CARBONIZATION

The coal was carbonized in 20-gram charges in a Vycor tube retort, set up as shown in figure 1. The central zone of the furnace could be maintained at the desired temperature $\pm 5^{\circ}\text{C}$. Dry, oxygen-free nitrogen was introduced into the retort to flush out the air at the start of each run, and a very slow stream of nitrogen was maintained during carbonization and cooling. After the furnace was charged, its temperature was raised at the rate of 5°C per minute until the selected final temperature was reached, and this temperature was held for 45 minutes.

The tar was collected at room temperature in the 100 ml distilling flask receiver (fig. 1) from which it was washed with acetone. The small amount that was deposited in the end of the retort was removed by swabbing with cotton moistened with the same solvent, and was then extracted from the swabs with more acetone. After the solvent had evaporated on the steam cone, six portions of about 50 ml of benzene were added and boiled off successively to remove water. Finally, the beaker containing the tar was kept in a desiccator over calcium chloride for several days.

TITRATION

The titration, a modification of that described by Moss, Elliott, and Hall (1948), was carried out in the apparatus shown in figure 2.

The sodium aminoethoxide titrant solution was prepared from clean sodium and monoethanolamine that had been carefully dried over sodium hydroxide pellets and triple distilled through a packed column. The sodium (2.5 grams) was washed with successive small portions of ethanol and monoethanolamine and dissolved in 100 ml of monoethanolamine (with cooling as necessary), made up to 500 ml with carefully purified anhydrous ethylenediamine, and standardized against U. S. Bureau of Standards pure benzoic acid.

The sample for titration was weighed out in a small weighing bottle, dissolved in 5 ml of benzene, transferred to the titration flask, and the bottle rinsed with another 5 ml portion of benzene that was added to the solution in the titration flask. Anhydrous ethylenediamine (40 ml) was added and the flask attached to the titration assembly. The antimony indicator electrode was polished and inserted, the magnetic stirrer started, and the electrodes were connected to the Leeds and Northrup student-type potentiometer that was used to measure the electromotive force (EMF). The reference electrode, which was immersed in the titrant solution below the stopcock of the buret, was also made of antimony, and the electrical circuit between the electrodes was completed through the side-arm just above the buret tip (fig. 2). The lower flared end of this side-arm was closed by a sealed-in, sintered glass plate and immersed in the solution in the titration flask.

After allowing at least one and a half hours for the system to attain equilibrium, the solution was titrated potentiometrically with the approximately 0.2 N sodium aminoethoxide solution. The titrant was added at the rate of 0.2 ml per

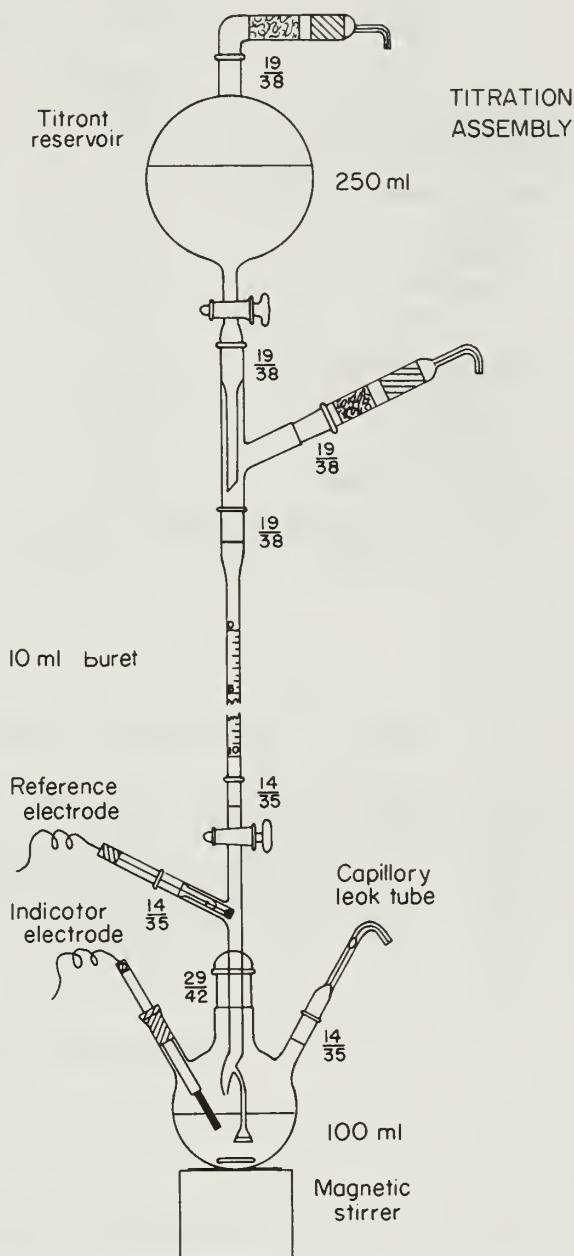


Fig. 2. - Titration assembly. "Fraction" notations designate standard taper joint sizes.

Table 1. - Analytical Data, Illinois No. 6 Coal, Knox County

	Percent		
Moisture (as rec'd)	14.3	Calorific value (d.a.f.):	
Volatile matter (d.a.f.)	49.4	Btu/lb	14382
Forms of sulfur (d.a.f.):		cal /g	7990
Sulfate	0.56	Gieseler plasticity:	
Pyritic	0.48	Softening temp.	353°C
Organic	<u>2.17</u>	Fusion temp.	391°C
Total	3.21	Max. fluidity temp.	415°C
Petrographic analysis:		Setting temp.	469°C
Vitrinite	95.5	Max. fluidity*	2320
Exinite	2.6	dial div /min	
Inertinite	1.1	Free swelling index	3.5
Mineral matter	0.8		

* Packed with 3 drops of benzene; swelled out of sample cup.

Table 2. - Analytical Data, Coal and Carbonization Products

Carb. temp., °C	Ash (dry)	Dry, ash-free basis						Tar**	Solid**	Solid product
		C	H	N	S	O*				
Coal	2.46	79.60	5.53	1.44	3.25	10.18	---	---	---	
200°	2.80	78.99	5.51	1.43	3.32	10.75	---	16.55	Unconsolidated	
300°	2.55	79.23	5.48	1.45	3.29	10.55	---	16.46	Unconsolidated	
350°	2.60	80.57	5.40	1.46	3.08	9.49	0.1386	15.78	Slightly consol- idated char; broke up on handling	
400°	2.93	82.58	4.66	1.59	2.72	8.45	1.9712	13.82	Very highly swollen soft coke; frothy texture	
450°	3.31	84.67	3.97	1.68	2.57	7.11	1.9835	12.11	Highly swollen soft coke; frothy texture	
500°	3.54	86.51	3.40	1.70	2.25	6.14	1.9673	11.48	Moderately hard, slightly swollen coke	
550°	4.95	87.36	3.05	1.71	2.19	5.69	1.9837	11.30	Hard, unswollen coke	
600°	4.69	89.08	2.65	1.70	2.21	4.36	1.9823	10.99	Hard, slightly shrunken coke	

* Oxygen percentage obtained by difference.

** Grams obtained from 20 grams of coal charged to the retort.

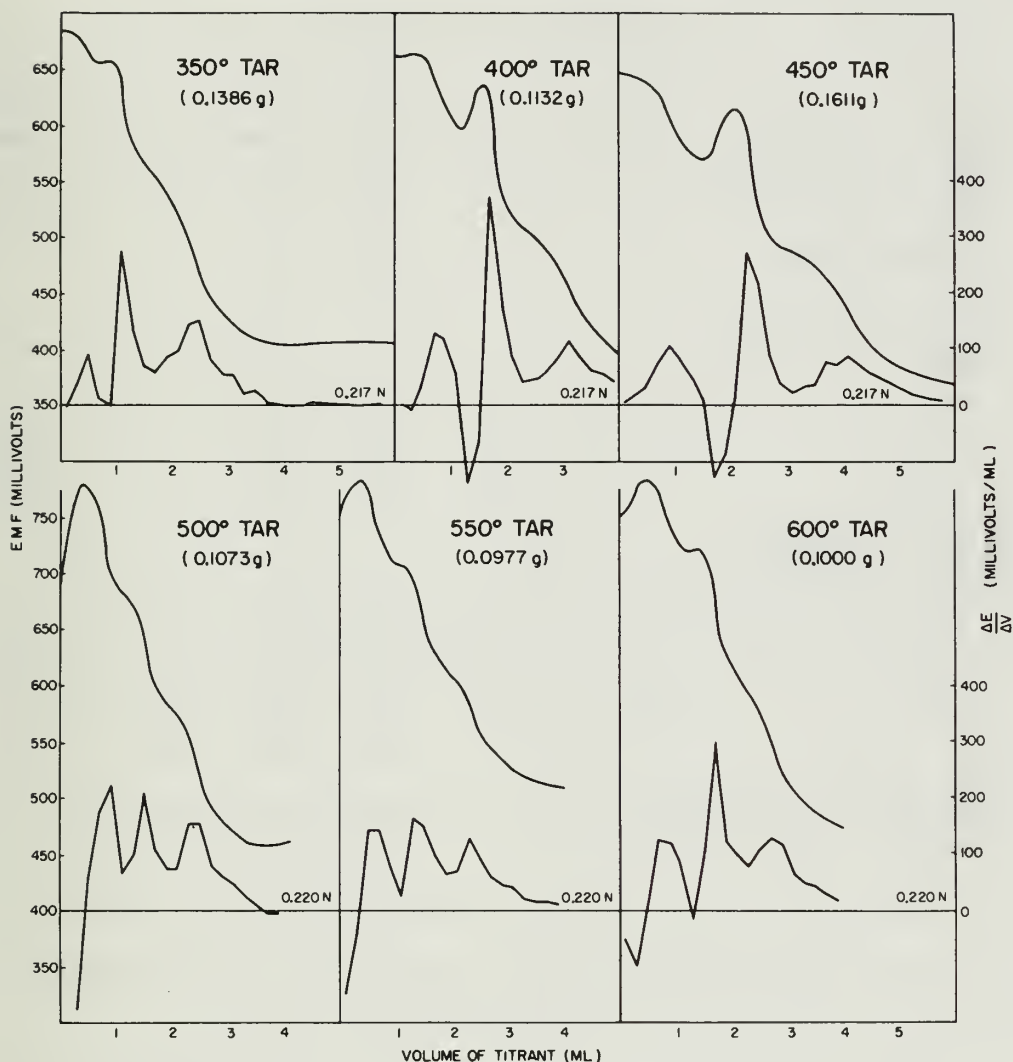


Fig. 3. - Titration curves and derived graphs.

minute. The electromotive force was plotted against the volume of the titrant added so that the endpoints appeared as inflections in the curve. The derived graph, in which the change of EMF per unit volume of titrant added is plotted against the volume added, shows the endpoints as peaks.

Additional details of the carbonization procedure, the titration method, the construction of the apparatus, and preparation of reagents are reported by Maher, Harris, and Yohe (1959).

RESULTS AND DISCUSSION

The tars were obtained from carbonizations at 350°, 400°, 450°, 500°, 550°, and 600°C. The analyses of the original coal and the chars and cokes from it are given in tables 1 and 2.

Table 3. - Titration Data

	350°	400°	450°	500°	550°	600°
Weight of tar (grams)	0.1386	1.9712	1.8935	1.9673	1.9837	1.9823
Total acidity (milliequivalents per gram)	3.54	5.66	5.29	4.74	5.00	5.74
"Equivalent weight"	282	177	189	211	200	174
Component acidities (milliequivalents per gram)						
Strongest	0.47	1.19	0.97	1.44	1.15	1.54
Medium	0.99	1.88	2.03	1.39	1.78	1.91
Weakest	2.08	2.59	2.29	1.91	2.07	2.29
Acidity of tar sample* (milliequivalents)						
Strongest	0.07	2.35	1.84	2.83	2.28	3.05
Medium	0.14	3.71	3.84	2.73	3.53	3.79
Weakest	<u>0.29</u>	<u>5.10</u>	<u>4.34</u>	<u>3.76</u>	<u>4.11</u>	<u>4.54</u>
Total	0.50	11.16	10.02	9.32	9.92	11.38

* Total acidities of the samples, that is, milliequivalents per gram multiplied by the weight of the tar in grams.

The titration curves and the derived graphs for the tars are shown in figure 3.

Each curve shows three inflections, but at 400° and 450°C there was a large rise in EMF after the first inflection and before the second. For the 600°C tar there was a small rise at the same position.

Table 3 gives the total acidities in milliequivalents per gram corresponding to the final inflections. It also gives the component acidities corresponding to the separate inflections in order of relative strength (that is, in the order of titration, which places the strongest component acidity first). The equivalent

Table 4. - Comparison of Stronger and Weaker Component Acidities

Component acidities in milliequivalents per gram	350°	400°	450°	500°	550°	600°
Stronger*	1.46	3.07	3.00	2.83	2.93	3.45
Weaker	2.08	2.59	2.29	1.91	2.07	2.29
Ratio (str./wk.)	0.70	1.19	1.31	1.48	1.42	1.51

* The strongest and medium acidities given in table 3 are combined here as the "stronger" component.

weight corresponding to the total acidity of each tar, the weight of tar obtained from the 20-gram coal charge at each temperature, and the component and total sample acidities (obtained by multiplying milliequivalents per gram by the tar sample weight) are also shown in table 3.

In figure 4 these last values are shown plotted against the carbonization temperatures.

At 350°C so little tar was produced that it is not surprising that the results are quite different from those of the other tars. The 350°C tar is not considered in the following discussion.

The weight of tar obtained was at a minimum at 450°C, but the total acidity, both as milliequivalents per gram and as total milliequivalents, showed a minimum at 500°C. The weakest component acidity showed a similar change with the temperature.

The strongest and medium component acidities were more irregular and appeared to be somewhat complementary. Perhaps the rise in the titration curve mentioned previously was caused by a solubilizing effect of the sodium ion, thus making available for titration more of the strongest groups, thereby giving rise to the second inflection.

In table 4 the values for strongest and medium component acidities are combined as a single "stronger" component acidity. Its variation was more regular, and it also had a minimum value at 500°C. The ratio of stronger to weaker groups, also shown in table 4, increased with the carbonization temperature.

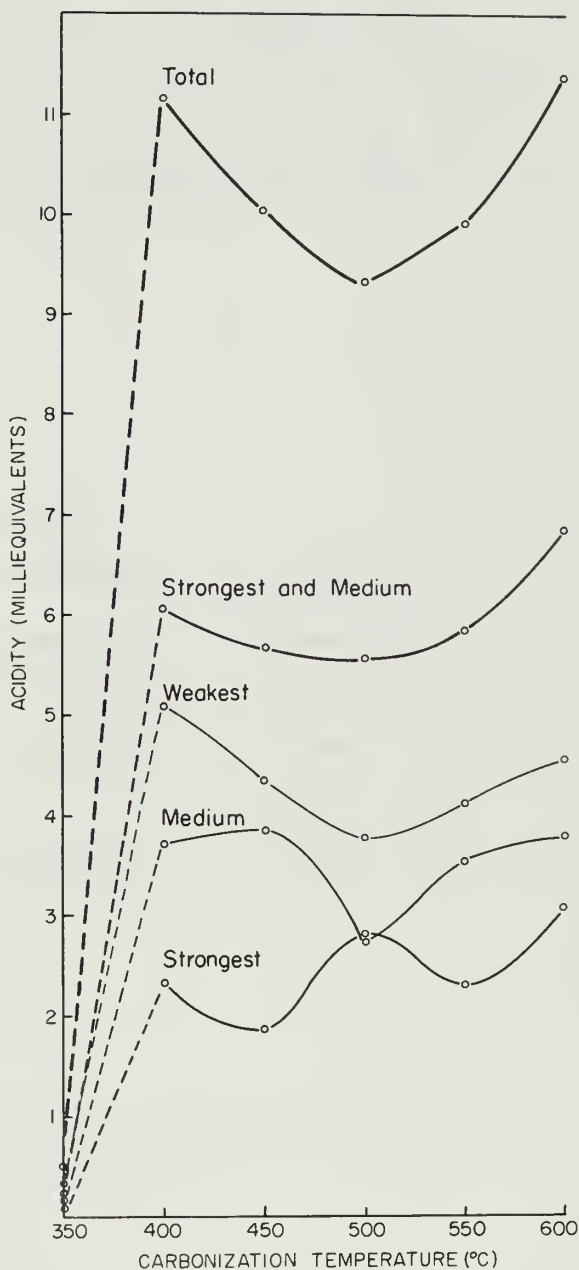


Fig. 4. - Changes in total and component acidities with carbonization temperature.

SUMMARY AND CONCLUSIONS

Titration with sodium aminoethoxide in ethylenediamine, when the necessary equipment and reagents are available, is a convenient method of determining acidic groups in coal tars.

In the series of tars from the high-volatile coal studied, groups of at least two distinct acidic strengths were found to be present. The ratio of the more strongly acid to the more weakly acid groups increased with increase in the carbonization temperature to 600°C.

The total and component acidities decreased from 400° to 500°C and then increased again as the carbonization temperature was raised to 600°C. At 350°C only a little tar of low acidity was obtained.

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