TITRATION OF ACIDIC FUNCTIONAL GROUPS IN COAL

By

W. E. Walker, J. P. Henry, and H. G. Davis

Union Carbide Olefins Company
Division of Union Carbide Corporation
South Charleston, West Virginia

ABSTRACT

    Titration of a large number of samples of whole coals, vitrains and
macerals with sodium aminoethoxide in ethylenediamine has been studied. The
procedure used differs from a previously published method in calling for
co-titration of coal samples with small amounts of the weakly acidic compound,
carbazole. This sharpens endpoints and allows titration of groups in coal
which consume titrant but do not otherwise give distinguishable inflections.
After correction for carboxyl, values for phenolic hydroxyl in coal agreeing
with the highest reproducible results reported by other methods are obtained.
The titration of hydroxyl and of other acidic groups which may be present
in coal has been studied.

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INTRODUCTION

Specific analytical methods are now available for determination of acidic hydroxyl groups in coal.[1,2,3,4,5] While there is general qualitative agreement among the several methods, quantitative differences remain, sometimes in the same method as applied by different laboratories. Particular procedures may require times ranging up to a day or more.[2] The need for a rapid and reliable volumetric method for determination of acidity has been apparent for some time.

Application to finely ground coal of the potentiometric titration of phenolic hydroxyl with sodium aminoethoxide in anhydrous ethylenediamine[6,7], has recently been reported by Brooks and Maher[8]. The present paper reports results obtained in this laboratory by a similar but in some respects significantly different procedure. After correction for carboxyl and possibly for certain other acidic groups of much less importance, the procedure appears to give reasonable values for total acidic OH over the range from brown coal to low volatile bituminous. Satisfactory agreement with the acetic anhydride method of Blom, et al.[2] is obtained.
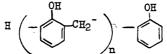
We have been able to obtain sharper endpoints and higher titration values by co-titration with a quantity of the weakly acidic compound carbazole.

This procedure has been of particular help with low rank coals such as lignites but also is useful in the low volatile bituminous range. With these coals it has been obvious in straight titration that titrant was consumed beyond the last clear break in the titration curves. The co-titration technique resolves the additional consumption into an easily discernible inflection. With specific coals giving sharp final breaks, little or no effect is noted. Carbazole has here the value of an indicator, although used in non-indicator quantities. All accessible functional groups of acidities down to the order of the acidity of carbazole are titrated at the carbazole endpoint.
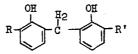
Other factors studied which have been shown to be of importance include the degree of subdivision of the coal sample and the rigid exclusion of oxygen as well as of carbon dioxide during titration. Particle size is especially important with coals of higher rank. Apparently in coals of 88-90 per cent carbon there is considerable OH in positions accessible to titrant only with great difficulty. Exclusion of oxygen plus the availability of a suitable grade of ethylenediamine has allowed us to titrate with satisfactory endpoints weak acids which have not been found titratable in some laboratories.

Interpretation of an overall acidity by titration of coal in terms of phenolic hydroxyl content requires a knowledge of the functional groups possibly present in coal and titratable by the ethylenediamine technique. There is now an excellent basis for the assumption that practically any carboxyl or phenolic hydroxyl group can be titrated within the potential range permitted by the carbazole endpoint. Monohydric phenols[7], and dihydrics show the expected equivalence as do amino phenols. We have, contrary to findings elsewhere[9,10], been able to titrate all OH in polyphenols of the type

$$H \left(-\underset{}{\bigcirc}\!\!\!\!\!\overset{OH}{}\!\!-CH_2^- \right)_n -\underset{}{\bigcirc}\!\!\!\!\!\overset{OH}{}$$

Both hydroxyls in hindered compounds of the type

$$R-\underset{}{\bigcirc}\!\!\!\!\!\overset{OH}{}-\underset{C}{\overset{H_2}{|}}-\underset{}{\bigcirc}\!\!\!\!\!\overset{OH}{}-R'$$

can be titrated if R and R' are n-amyl, substitution of bulky t-butyl groups being required to reduce the apparent equivalence to one; thus we could titrate only one equivalent in 2,2' dihydroxy-3,3',5,5'-tetra-t-butyldiphenylmethane. Both OH groups can be titrated in such compounds as 2,2'-dihydroxy-1,1'-binaphthyl.

Esters formed between carboxylic acids and phenolic OH undergo solvolysis and consume an equivalent of titrant[11]. Lactones of phenolic OH behave similarly[11].

Carboxyl and phenolic hydroxyl thus constitute the major acidic functional groups in coal which it should be possible to titrate quantitatively in ethylenediamine if they can be rendered accessible to titrant. Since carboxyl can be separately determined by a relatively simple method (cf. ref. 2 or 3 for review), and is of minor importance except in coals of low rank, a value of COOH + OH can be corrected for COOH to give a net value for phenolic OH.

It remains to estimate how much titer is consumed by the other titratable structures which may be considered as interfering groups in a phenolic hydroxyl determination. A fairly extensive study of functional groups which react as acids in this system has been made and will be published separately. Where no other reference is given below, the result has been obtained in this study. Groups which require consideration include:

1. Other acidic oxygen groups. Enolic forms of ketones, etc. may interfere but can be of no importance except possibly in the lowest rank coals or in peat. Quinone oxygen appears to be present to some extent in coal, but the amount is uncertain (ref. 2) and there is evidence against the presence of any large quantity.[12] Experiments with simple quinones indicate that they appear as weak acids in the ethylenediamine titration consuming one (acenaphthaquinone) or two (paraquinone, 1,4-naphthoquinone) equivalents of titrant per mole. The shape of the titration curves obtained is abnormal and indicates that chemical reaction proceeds during titration. Quinones in coal will therefore interfere, but the extent of the interference is probably quite small. Other types of carbonyl compounds do not in general interfere.

2. <u>Acidic Sulfur</u>. Coals of high organic sulfur content show total acidities comparable to those of other coals of the same oxygen content. The contribution of acidic sulfur (thiophenol and mercaptan) to the total titer of more typical coals low in organic sulfur must be exceedingly low.

3. <u>Acidic Nitrogen</u>. Titration of indole and carbazole in ethylenediamine shows them to be weak acids giving definite endpoints corresponding to consumption of one equivalent of titer per mole of compound. Pyrrole itself is too weakly acidic to react. There is reason to believe that much of the nitrogen in coal is basic. If the results[13] of titration in acetic acid with perchloric acid are calculated as nitrogen, roughly half the nitrogen may be accounted for in bituminous coals. While not all of the remaining nitrogen is both acidic and accessible to titrant, the necessary correction may still be appreciable, perhaps up to 40 per cent of the contained nitrogen. For a typical coal with 1.5 per cent N the correction for acidic N would then be of the order of -0.2 ± 0.2 milliequivalents per gram. Like OH, acidic NH probably becomes less important in very high rank coals.

We have found that N-phenyl and ∝-phenyl amides (benzamide, acetanilide, formanilide, benzanilide) can be titrated as weak acids in this system. They give definite endpoints corresponding to consumption of one equivalent of titrant per mole.* Such structures may be present but are not likely to be of importance in coal.

4. <u>Hydrocarbons</u>. One compound, 1,2-benzfluorene is the only one of many

hydrocarbon structures tested which reacted as a weak acid in ethylenediamine. Fluorene and 2,3-benzfluorene could not be titrated and indeed the 1,2 isomer can be determined quantitatively in their presence by titration. The chance that any significant amount of titratable C-H exists in coals appears to be remote.

Except possibly for quinone the total contribution to the determined acidity of all groups other than COOH, phenolic OH and their esters and lactones should never be greater than 0.6 milliequivalents per gram except conceivably in the lowest rank coals. More probably it is of the order of half this. In high rank coals, where nitrogen and sulfur, like oxygen, are in unreactive or inaccessible forms this contribution should be much less.

<center>APPARATUS AND PROCEDURE</center>

An automatic feeding and recording titrimeter was found to be convenient, rapid and reproducible for titrations in ethylenediamine. The titration was run in a one-piece 5-neck vessel of about 60-70 ml. capacity. Two larger necks served for insertion of electrodes which rested on rubber collars. The two smaller connections to the vessel served as nitrogen inlet and outlet. The outlet was vented to a hood to avoid toxic fumes and the deposit of electrically conducting films. The fifth neck was a 10/30 standard taper joint fitted with a capillary tube for addition of titrant.

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* Titration of certain amides as bases in acetic anhydride has been reported by D. Wimer[14]. It is interesting that the particular amides which appear as acids in the ethylenediamine titration do not react as bases in acetic anhydride.

The titrant feed system consisted of an accurately calibrated 10 cc. hypodermic syringe mounted on a heavy iron base and driven through special connectors by the gear box of a Monodrum Recording Apparatus. The outlet end of the syringe was then connected to the capillary tubing leading to the titration vessel.

The electrodes employed for the titrations were a Beckman Type E, high pH glass electrode and a Leeds and Northrup platinum sheet electrode. In this system the glass electrode was the reference electrode while the platinum electrode served as the indicating electrode. The electrodes were connected to a Leeds and Northrup line-operated pH meter which was in turn connected to a Leeds and Northrup strip chart recorder. An upscale-downscale adjuster allowed linear recording of a particular potential range desired (usually -100 to +900 millivolts). Distance along the chart paper was calibrated so as to be interpretable in milliequivalents of titrant added. The titrant feed rate for coal titrations was usually about 0.06 milliliters per minute of 0.2 N sodium aminoethoxide, with an ordinary titration consuming 1.0-1.5 milliliters of titrant.

In the usual titration procedure, the completely fitted titration vessel was flushed with high purity nitrogen. One electrode was removed and ethylenediamine was added from its storage bottle using nitrogen pressure. Titrant was then added until an inflection occurred indicating that the CO_2 contained in the ethylene-diamine had been neutralized. Then, with stirring stopped and a strong nitrogen flow through the vessel, the electrode was again removed and the coal sample added. The electrode was thoroughly rinsed and dried and reinserted into the titration vessel. After a 5-minute stirring period the titration was begun. Stirring of coal samples for various lengths of time up to 30 minutes resulted in no noticeable change in titer values so that shorter times were generally used.

The approximately 0.2 N sodium aminoethoxide was prepared in the usual way by reacting sodium with monoethanolamine and diluting with anhydrous ethylenediamine. Both the ethanolamine and the anhydrous ethylenediamine (Union Carbide Chemicals Company), were used as received. Attempts to treat the ethylenediamine, such as distillation or treatment with sodium or sodium hydroxide, while removing the CO_2, resulted in contamination with oxygen and other weakly acidic impurities which were more nuisance than the CO_2. It was found simple and preferable to neutralize the CO_2 by titration.

When ethylenediamine containing no dissolved oxygen was pumped directly from its original container to the titrating vessel with nitrogen pressure, and a blank titration run, the inflection at the CO_2 endpoint was 600-700 millivolts with the entire curve covering a span of about 1000 millivolts. When oxygen was present it was removed by bubbling nitrogen through the ethylenediamine. The mechanism of the effect of dissolved oxygen is not known. However with the electrode system employed, the oxygen acts as a buffer, shortening the millivolt span by about 300 millivolts in the weak acid region. Also the removal of dissolved oxygen by the purge nitrogen during titration can result in a sharp inflection easily misinterpreted as the end-point for a weak acid. Best results were obtained by keeping oxygen-free ethylene-diamine under a flow of oxygen-free* nitrogen, and by using similar nitrogen during titrations. The most weakly acidic compounds cannot be titrated satisfactorily unless oxygen is rigidly excluded. Some of these effects of oxygen were first noted and pointed out to us by Dr. H. Tschamler[15].

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* Commercial high purity nitrogen (Linde Company) further purified by passage over hot copper chromite.

RESULTS AND DISCUSSION

In general coal samples can be handled in very much the same way as pure organic chemicals. Special attention must, however, be given to particle size, since coals are of limited solubility and the neutralization reaction may be largely homogeneous. A second problem found with coals is that they contain functional groups of a wide range of acid strengths. As a result, particular coals may give several small inflections and consumption of titrant may be evident beyond the last recognizable endpoint. Coals of very low rank especially give titration curves of this type. Coals with > 88 per cent C may show very weak titration inflections together with a potential slope generally indicating consumption of titer.

The effect of particle size was studied by comparing samples ground more or less extensively. Table I shows results obtained with seven whole coals or vitrains of various ranks.

TABLE I

EFFECT OF PARTICLE SIZE ON TITRATION

| | | Titer, Meq./gram (d.a.f.) | | |
Coal	% C	-200 Mesh	6-8 Hr. Grind 2-5 Micron	30 Hour Grind
Beckley Seam	89.7	0.035	0.23	0.65
South Garesfield Victoria, Durham	88.9		0.54	1.15
Sneyd Cockshead, Staffordshire	86.1		1.93	2.15
No. 2 Gas Seam	83.5	1.84	2.33	
No. 5 Block	82.1	1.75	2.19	
Ellington High Main, Northumberland	81.1		2.92	2.86
Pittsburgh No. 8	80.0	2.58	2.83	

All grinding was done under nitrogen atmosphere. Grinding to pass a 200 mesh USS sieve is not sufficient even at 80 per cent C. Six to eight hours of dry ball-milling with a high ratio of ceramic balls to coal proved satisfactory at 81 per cent C and nearly so at 86 per cent C. Increasing milling time to 30 hours failed to increase the titer at 81 per cent C, increased it slightly at 86 per cent C and caused substantial increases at 88-90 per cent C. The 6-8 hour samples had average particle sizes of about 2-5 microns with a few particles over 10 microns in diameter. It is of course possible that still more severe size reduction would further increase the titer at 90 per cent C. There appears to be a range of coal ranks in which acid functional groups are present but are accessible to chemical reactants only with great difficulty. Exploration of the particle size effect on other functional group determinations seems desirable.

The second difficulty was solved by adding a weakly acidic substance to the coal samples before titration. Carbazole in ethylenediamine is an acid about as weak as the weakest of the phenolic hydroxyl types which have been found titratable. When sufficient carbazole is added to a coal sample, the final inflection in the potentiometric titration curve appears at roughly the same potential as the endpoint for carbazole alone and is sharp enough to be readily identificable. Correction for an amount of titrant equivalent to the amount of carbazole added gives a net amount of titrant consumed by the coal. This amount is generally greater than obtained by direct titration.

Table II shows the magnitude of the increase in titer value. The effect is arithmetically greater in the range where this might have been predicted from the shape of the titration curves, that of very low ranks (< 80% C). However, coals of all ranks show increase and the percentage increase is actually greatest at high ranks (> 88% C). Very fine grinding sharpens the endpoints obtained with coals sensitive to grinding, and reduces the difference between the values obtained with and without carbazole.

Typical potentiometric titration curves for a coal with and without carbazole and for meta cresol are shown in Figure 1.

TABLE II

EFFECT OF CARBAZOLE ADDITION ON TITER VALUE OF COALS

Coal	% C	6-8 Hr. Grind		30 Hr. Grind	
		Direct Titration	With Carbazole	Direct Titration	With Carbazole
Pocahontas No. 3 (vitrain)	91.0	0.185	0.262		
Beckley Seam	89.7	0.23		0.65	0.89
South Garesfield Victoria, Durham	88.9	0.54	1.18	1.15	1.39
Sewell Seam (vitrain)	88.6	0.631	0.957		
Sneyd Cockshead, Staffordshire	86.1	1.93	2.50	2.15	2.64
Pittsburgh No. 8 (vitrain)	84.6	2.83	3.32		
Pittsburgh Bed (vitrain)	84.7	2.71	3.12		
Illinois No. 6 High Vol. B (vitrain)	82.4	3.26	3.79		
Ellington High Main, Northumberland	81.1	2.92	3.71	2.86	3.72
Illinois No. 6 High Vol. C (vitrain)	80.1	4.13	4.70		
Pittsburgh No. 8	80.0	2.83	3.48		
North Dakota Lignite	70.9	4.24	5.45		
Texas Lignite	70.8	3.45	6.17		
German Brown Coal	66.9	3.56	6.55		
Brown Coal Zentraltagbau Köln	67.6	3.45	5.45		

The results tabulated above have been obtained either with vitrains containing a high proportion of the maceral vitrinite or with whole coals. Most of the latter have been bright coals relatively high in vitrinite. Professor C. Kröger, Institute of Fuel Chemistry, Technical University, Aachen, Germany, kindly gave us samples of the individual macerals he has recently separated from four German coals by a special technique[16]. With these materials it has been possible to compare the behavior in titration of the petrographic constituents of coal.

Since the samples of macerals were quite small a less efficient grinding technique (rotation with glass beads in a small glass bottle) was substituted for the usual ball-milling. This may have reduced the determined acid value somewhat, especially for the vitrinite of highest carbon content. The titration results* are given in Table III together with the carbon and oxygen determinations reported by Kröger, et al[17]. With reliable direct oxygen determinations available, it is possible to plot acidity in milliequivalents per gram versus weight per cent O in Fig. 2.

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* Some of these results were discussed by Professor Kröger at the Second International Conference on Coal Science, Falkenburg, Netherlands, May 1957.

Apparently we have been able to account for a high percentage of the O as acidic in the vitrinites of the three coals of lower rank, and a somewhat smaller per cent of the O in the micrinites. The micrinite curve is, however, similar to the vitrinite. The exinites behave differently, the determined acidity for the four samples being essentially independent of either rank or total oxygen content. The same conclusion was reached by Kröger, et al.[17] on the basis of a hydroxyl determination.

This result is of interest in connection with estimates of the aromaticity of the various macerals which have been made[17] from density measurements and ultimate analyses. The exinite of highest carbon content (Wilhelm) was calculated to be of the same degree of aromaticity as the corresponding vitrinite. The other three exinites are considerably less aromatic than the corresponding vitrinite. In order of decreasing carbon content the percentage of the carbon atoms estimated by Kröger et al. to be in aromatic rings is:

Seam	Vitrinites	Exinites
Wilhelm	75	77
Anna	76	70
Zollverein	76	62
R	72	52

It is reasonable to suppose that the additional oxygen present in the lower rank exinites is non-acidic because it is present in non-aromatic structures.

TABLE III

TITRATION OF PURE MACERALS

Seam and Fraction	% C*	% O*	Titer Value, meq./gram (d.a.f.)			
			No Carbazole		With Carbazole	
				% of Total O Recovered as OH		% of Total O Recovered as OH
Wilhelm						
Vitrinite	88.8	4.0	0.24	10	0.40	16
Exinite	89.3	3.8	1.12	47	1.20	51
Micrinite	89.8	4.5	0.93	33	0.99	35
Anna						
Vitrinite	88.4	4.7	1.30	44	1.73	59
Exinite	89.1	3.8	0.92	39	1.04	44
Micrinite	89.6	5.0	0.97	31	1.07	34
Zollverein						
Vitrinite	85.7	7.8	2.18	45	Insufficient sample	
Exinite	87.4	4.7	0.93	32	0.91	31
Micrinite	88.0	6.8	1.70	40	1.72	40
R						
Vitrinite	83.4	9.8	2.95	48	2.94	48
Exinite	85.5	5.8	1.01	28	0.97	27
Micrinite	86.8	8.1	1.77	35	2.02	40

* Analyses from paper of Kröger et al, ref. (17).

Ultimate analyses of the whole coals and vitrains studied are given in Tables IV and V.

TABLE IV

ULTIMATE ANALYSES[*]

VITRAINS AND COALS OF KNOWN VITRINITE CONTENT

	C	H	N	S	Per Cent Vitrinite	O[**] Meq./g.
Vitrains						
Pittsburgh Bed, Bruceton, Pa.	84.7	5.6	1.8	0.4	92.0	5.19
No. 6 Bed Illinois High Volatile C	80.1	5.3	1.2	2.4	95.5	8.19
No. 6 Bed Illinois High Volatile B	82.4	5.4	1.6	1.3	95.7	6.75
Pittsburgh No. 8	84.6	5.4	1.4	0.4	93.4	5.31
Sewell Seam, Skelton Mine	89.9	5.0	1.8	0.3	94.1	2.06
Beckley Seam, Low Volatile	90.2	4.9	2.0	0.2	94.0	1.94
Sewell Seam, Garden Ground Mine	88.6	5.0	1.8	0.6	96.0	2.75
Pocahontas No. 3, Buckeye No. 3 Mine	91.0	4.8	1.3	0.6	95.0	1.63
Whole Coals[***]						
DIII, Ellington High Main, Northumberland	81.1	5.1	2.0	1.1	85.4	7.55
DIX, Sneyd Cockshead, Staffordshire	86.1	5.5	2.2	0.7	77.7	4.37
DXIII, South Garesfield Victoria, Durham	88.9	5.1	1.6	0.8	88.6	2.56

[*]   Analyses obtained under the supervision of Mr. Saul Gottlieb of this laboratory; percentage vitrinite in vitrains by Mr. A. N. Kurtz.

[**]   From oxygen-carbon relationship of van Krevelen and Chermin.[18]

[***] These samples supplied by Dr. W. F. Wyss, British Coal Utilization Research Association, Leatherhead, Surrey; percentage vitrinite reported by I.G.C. Dryden.[19]

TABLE V

WHOLE COAL ANALYSES (d.a.f.)

	C	C (Parr)	H	N	S	Titer Value Meq./g.	Titer Value Meq./g. Carbazole Added
Beckley	89.7	90.8	4.9	1.5	0.8	0.23	
No. 5 Block	82.1	84.1	5.8	1.3	1.1	2.19	
No. 2 Gas	83.5	85.0	6.0	1.5	1.0	2.33	
Pittsburgh No. 8	80.0	82.6	5.9	1.5	3.4	2.83	3.48
Pittsburgh Bed	84.3	85.0	5.8	1.6	0.8	1.96	
Middle Kittanning	81.2	82.0	5.9		0.7	2.92	
No. 5 Bed Indiana	80.0	82.1	5.8		3.1	2.58	
German Brown Coal	66.9	70.0	5.2	0.8	6.4	3.56	6.55
Sewell Seam	89.4	89.8				0.53	
Texas Lignite	70.8	72.6	5.2	1.7	2.5	3.45	6.17
N. Dakota Lignite	70.9	71.7	4.7	1.3	0.7	4.24	5.45
Fulton Bed	90.6	91.6	4.9		0.8	0.08	
Jedo Anthracite	94.1	95.3	2.4	0.8	0.5	0.09	
Zentraltagbau Frechen/ Köln, Brown Coal	67.6		4.7	1.0	0.4	3.95	5.45

Accurate estimates of the oxygen contents were not generally available. As an indication of the effect of oxygen content and rank, we have plotted for the coals of Table IV, measured acidity versus percentage of carbon (Figure 3). The curve drawn in the figure is the line of total oxygen content (right-hand axis) or 50 per cent titration of contained oxygen (left-hand axis) based upon a standard relation between oxygen and carbon content for vitrain[18]. The values obtained with samples ball-milled 6-8 hours were used for the plot.

By titration with added carbazole, 50 per cent or more of the oxygen in bituminous vitrains of from 80-86 per cent C can be accounted for as phenolic OH. Generally the recovery as OH is of the order of 60 per cent. From a reasonably accurate oxygen by difference estimated for the sample at 82 per cent C, it seems probable that the recovery here is also nearly 60 per cent instead of 50 per cent as plotted. Additional grinding of the sample of 89 per cent C raised its titer to 1.39 milliequivalents per gram indicating better than 50 per cent O as OH even at this rank. In the range 89-91 per cent C only a small percentage of the O can be accounted for as acidic OH either because of inaccessibility to titrant or because the oxygen is in a non-acidic form.

COMPARISON WITH LITERATURE

Figure IV shows a comparison between the results of the present work and those of Brooks and Maher[8]. Here percentage of oxygen titrated is plotted against carbon content. Again we have used the standard relationship between oxygen and carbon analysis rather than the somewhat uncertain oxygens by difference available. The points in the region of lowest rank have been corrected upward for the presence of carboxyl (two oxygen atoms per equivalent). The carboxyl values used were from the relation of Blom, et al. (ref. 2, Fig. 3). An exception is the German brown coal plotted at 67.6 per cent C. A value of 1.84 milliequivalents per gram determined in this laboratory was used rather than 2.1 read from the curve given by Blom.

The results of this laboratory lie substantially above those of Brooks and Maher over much of the range of carbon contents studied. The tabulated data (Table II) show that this difference is largely explainable on the basis of our titration of more weakly acidic groups with the aid of carbazole. The two curves approach each other at the high carbon end. If we had plotted our direct titration values, we could have represented both sets of data fairly well with a single curve. Both curves of Figure 4 have essentially the same shape and both indicate a maximum in the percentage of contained oxygen titratable at about 85 per cent C.

That the higher values obtained by using carbazole are reasonable is indicated by Figure 5. Here titratable acidity in milliequivalents per gram has been plotted against ultimate carbon content for a wide variety of vitrains and whole coals. On the same graph we have plotted milliequivalents of OH plus COOH as reported by Blom, et al.[2] For OH content Blom's higher value based upon acetylation with acetic anhydride in pyridine was used. The agreement over the entire range of carbon contents between the titration results obtained with carbazole and Blom's acetylation results is quite satisfactory.

Again the importance of carbazole is particularly evident in the lignite-brown coal region. The slight hump in the slope at about 85 per cent C indicated by both acetylation and titration data corresponds to the maximum in percentage of oxygen titratable as acid (Fig. 4).

As was pointed out in the introduction, analysis of OH in coal by various methods of functional group analysis has given somewhat discordant results. Figure 5 indicates reasonable agreement between the present results and those of Blom, et al.[2] Agreement with Ihnatowicz's[1] results obtained by exchange with Ba(OH)$_2$ is fair for coals of low carbon content. Results by other methods such as methylation with diazomethane are generally lower than the titration value. The very interesting trimethylsilyl ether procedure of Friedman, et al.[5] has not as yet been carefully cross-checked with the ethylenediamine titration. The results presented in September 1957[5] show 38 to 47 per cent O accounted for as OH in the range 81-88 per cent carbon (5 coals, one vitrain) averaging 43 per cent. This compares with an average of slightly below 60 per cent for vitrains titrated with carbazole. The fact that we are comparing results obtained with vitrains to results obtained mainly with whole coals may account for some of the difference. There is hope that careful cross-comparison on the same samples will reconcile more closely the two methods of analysis or determine reasons for the differences.
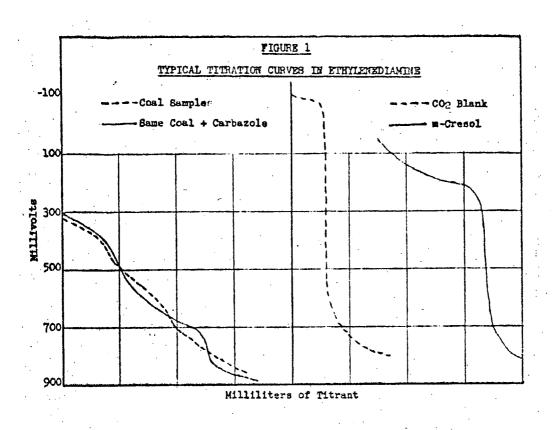
CONCLUSIONS

Titration of coal in ethylenediamine with sodium aminoethoxide titrant and in the presence of a weakly acidic substance such as carbazole offers a rapid, relatively simple method of determining a value of total acidity. After correction for carboxyl content a value for acidic hydroxyl is obtained agreeing well with the highest reproducible values reported by more specific methods of functional analysis. The percentage of total oxygen in coal determinable as acidic oxygen has a maximum at about 85 per cent C. The state of subdivision of samples titrated is extremely important with coals of carbon content above 88 per cent. The type of oxygen in coals is related to the petrographic analysis, especially to the proportion of the maceral exinite present.

A study has been made of the titration of functional groups which are possibly present in coal. Besides carboxyl and phenols of several types, a number of other groupings have been found to react as weak acids. Types not previously reported include certain polyphenols, indole and carbazole nitrogen, n-phenyl and α-phenyl amides and 1,2-benzfluorene. Quinones react and consume titer. The total contribution to the titer of all groups other than carboxyl, phenol and possibly quinone is believed to be low. The importance of rigid exclusion of oxygen in the titration of very weak acids in ethylenediamine was noted.
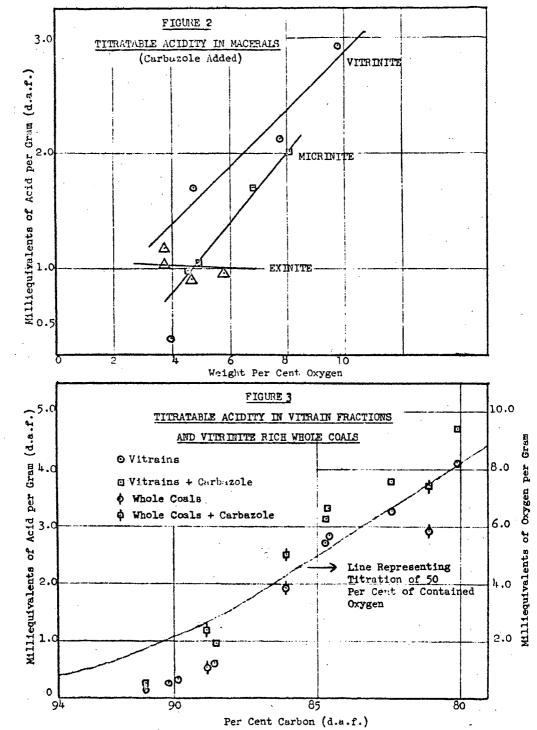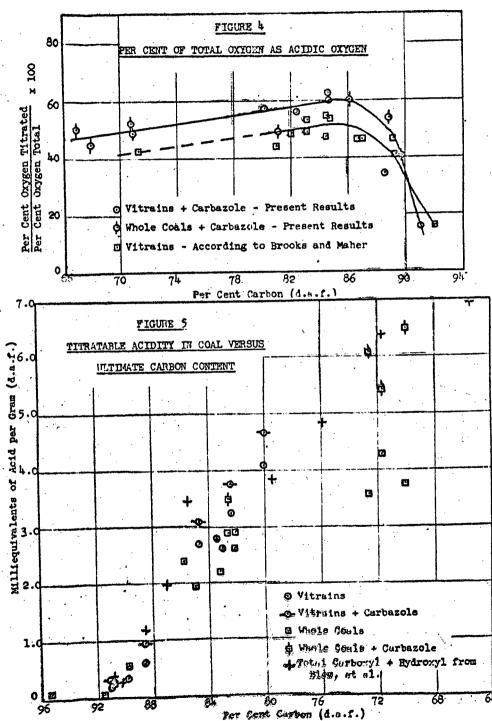
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FIGURE 1

TYPICAL TITRATION CURVES IN ETHYLENEDIAMINE

FIGURE 2

TITRATABLE ACIDITY IN MACERALS
(Carbazole Added)

VITRINITE

MICRINITE

EXINITE

FIGURE 3

TITRATABLE ACIDITY IN VITRAIN FRACTIONS

AND VITRINITE RICH WHOLE COALS

⊙ Vitrains

⊡ Vitrains + Carbazole

φ Whole Coals

φ Whole Coals + Carbazole

Line Representing
Titration of 50
Per Cent of Contained
Oxygen

FIGURE 4

PER CENT OF TOTAL OXYGEN AS ACIDIC OXYGEN

⊙ Vitrains + Carbazole - Present Results
◊ Whole Coals + Carbazole - Present Results
▣ Vitrains - According to Brooks and Maher

Per Cent Carbon (d.a.f.)

FIGURE 5

TITRATABLE ACIDITY IN COAL VERSUS

ULTIMATE CARBON CONTENT

⊙ Vitrains
◑ Vitrains + Carbazole
▣ Whole Coals
⊡ Whole Coals + Carbazole
✛ Total Carboxyl + Hydroxyl from
    Blom, et al.

Per Cent Carbon (d.a.f.)