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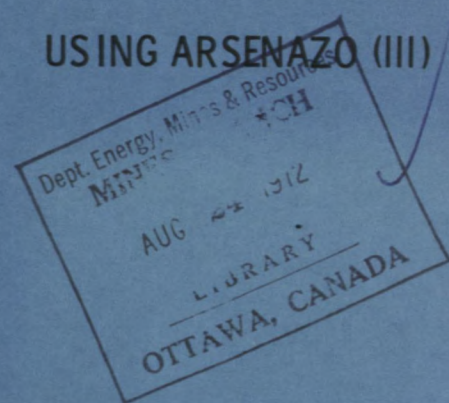
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ANALYSIS OF TOTAL SULPHUR IN CANADIAN
COALS BY A MODIFIED OXYGEN-FLASK METHOD

USING ARSENAZO (III)



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Analysis of total sulphur in Canadian coals by a modified oxygen-flask method using Arsenazo (III)

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A modified oxygen-flask method for total sulphur analysis using Arsenazo (III) as titration indicator and Chromel 'A' wire as combustion-grate material has been used to analyse twelve Canadian coals of widely differing rank, ash, and sulphur content. The results indicate that the method is generally applicable to coal sulphur analysis. The end-point unlike that of Thorin is sufficiently definite to permit use of the method by relatively untrained analysts. The precision of the method appears to be similar to that of the Eschka method.

The oxygen-flask (Schöniger) method has been in limited use for several years in determining total sulphur in coals and other organic compounds¹⁻⁶. A variation of the method is also used to determine halogens, particularly chlorine in coal⁷. The method has advantages in requiring only relatively simple and readily available equipment; for control analyses and for small numbers of analyses, the method is much less time-consuming than the well-known Eschka method.

The regular oxygen-flask method for sulphur analysis involves burning a small (150 mg) sample in oxygen at atmospheric pressure in an Erlenmeyer flask. The finely-ground sample is held in an envelope of ashless filter paper; the envelope is supported in a wire mesh or spirally wound wire 'grate' suspended in the centre of the flask. The combustion gases are absorbed in a solution of hydrogen peroxide contained in the flask and are finally titrated with barium perchlorate using Thorin [2-(2-hydroxy-3,6-disulpho-1-naphthylazo)-benzenearsonic acid] as indicator.

The method, using Thorin, for the analysis of coals has been described in detail by Ratcliffe and Cunningham² and

by the British Coke Research Association¹ but has not been widely used because the Thorin end-point is so indistinct that only with considerable practice can reliable results be obtained^{8,9}, thus restricting its use to experienced analysts. Moreover the end-point is transient and for accurate results and precise repeatability, small timed increments of titrant are required near the end-point¹⁰.

Hozumi and Umemoto⁸ found that by using Arsenazo (III) (1,8-dihydroxynaphthalene-3,6-disulphonic acid-2,7-bis [(azo-2)-phenylarsonic acid], sodium salt) instead of Thorin in the analysis of pure organic sulphur compounds, a distinct reversible end-point was obtained. Initial oxygen-flask sulphur analyses of coal modified by using Arsenazo (III), reported earlier¹¹, compared favourably with those obtained by the Eschka method. Because these analyses were confined to two coals, it was important to test the method for general applicability to Canadian coals. For this part of the study, twelve Canadian coals were chosen as representing the widely varying ranks and sulphur and ash contents of coals occurring in Canada. The coal samples are identified in *Table 1*.

Table 1 Identification of coal samples

Sample No.	Mine	Coalfield area	ASTM rank	Fixed carbon (% d.a.f.)
1	Cape Breton Development Corporation - No.26	Sydney, N.S.	High volatile A bituminous	59.1
2	Springhill Coal Mines, Limited	Cumberland, N.S.	High volatile A bituminous	61.3
3	Drummond Coal Company, Limited - No.1	Pictou, N.S.	Medium volatile bituminous	67.9
4	Acadia Coal Company - McBean	Pictou, N.S.	High volatile A bituminous	67.2
5	M & S Coal Company, Limited	Bienfait, Sask.	Lignite	54.4
6	Battle River Coal	Estevan, Sask.	Lignite	54.5
7	The Kleenbirn Collieries, Limited	Brooks, Alta.	Sub-bituminous B	57.2
8	The Canmore Mines, Limited	Cascade, Alta.	Low volatile bituminous	87.7
9	Battle River Coal	Sheerness, Alta.	Sub-bituminous C	55.2
10	Subway Coal, Limited	Drumheller, Alta.	Sub-bituminous B	56.7
11	Charter Coals	Drumheller, Alta.	Sub-bituminous B	57.2
12	Kaiser Resources, Limited	East Kootaney, B.C.	Medium volatile bituminous	79.1

EXPERIMENTAL

Combustion of the sample was done essentially as before¹¹, on samples ground to minus 60 mesh B.S. Several tests were made with coals of 0.5, 1, and 2% sulphur on samples ground to minus 200 mesh with no noticeable improvement in repeatability. Absorption times less than the 30 minutes mentioned earlier may be possible since it has been shown, in the oxygen-flask determination of chlorine in organic compounds, that absorption of the combustion gases occurs long before the 'fog' disappears¹². Because of the wide variation of time allowed for the absorption step^{1,2,8,13}, further work will be required to resolve the minimum time required.

Both direct and back-titration procedures were used. In the back titration, excess barium perchlorate was titrated with standard sulphuric acid. This latter procedure is much more rapid by virtue of the more stable end-point as noted elsewhere⁸. Moreover we found that the necessity to adjust pH before titration was eliminated. Preparation and description of reagents, procedure, and calculation are shown in Appendix I.

Combustion grate

One factor of importance in the combustion part of the method is the shape and size of the wire grate used as a sample container. In the original version of the oxygen-flask method, a platinum gauze or helical wire grate was used and apparently served as both sample support and combustion catalyst. However, it was shown that, in the combustion of inorganic sulphides, Chromel 'A' alloy wire promoted more efficient combustion than platinum and was better able to withstand the vigorous shaking in the absorption step¹⁴. The grate design is shown in *Figure 1*. The gauge of wire was found to be important in that too coarse a wire will inhibit combustion by cooling effects, whereas too fine a wire will cause mechanical instability. The best size of wire was found to be 18 SWG (1.22 mm). The optimum spacing between the successive turns of wire was found to be 0.30 to 0.45 mm. Too wide a spacing will permit particles of the sample to fall through the grate before being completely burned, and too close a spacing will restrict access of oxygen to the sample and cause incomplete combustion. The depth and inside diameter of the cylindrical section was 12.7 and 11.7 mm, respectively.

A hand-rotated mandrel to facilitate the preparation of wire grates was made (Appendix II) and was found capable of making uniformly sized grates rapidly and easily in the laboratory.

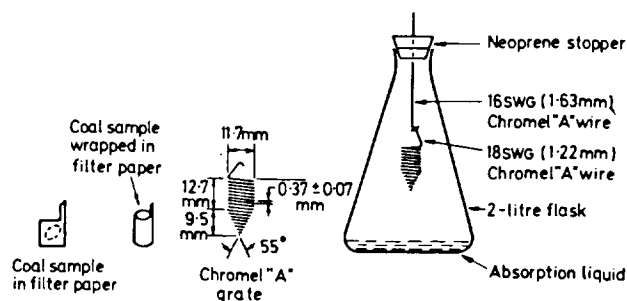


Figure 1 Combustion apparatus for modified oxygen-flask method of total sulphur analyses of coal

Removal of metallic ions

Because Arsenazo (III) reacts with metallic ions with consequent end-point difficulties when analysing for sulphate ions, the interfering metallic ions were removed by ion exchange. The volume of the ion exchange effluent was usually kept to 100 ml or less. The necessity to restrict the volumes in the rinsing and ion-exchange steps is related to the convenient volume of the solution to be titrated and depends upon the sulphate concentration of the combustion solution, as will be discussed later.

The effect of isopropyl alcohol

In the titration of the sulphate ion in aqueous solution by barium perchlorate using Arsenazo (III), no end-point is observed but one is obtained by adding isopropyl alcohol⁸. However, the end-point is not distinct until the solution contains at least 40% of alcohol and maximum distinctness is not obtained until the alcohol content reaches 80–90%. This amount of alcohol limits the amount of aqueous solution that can be titrated conveniently.

The effect of pH and concentration of indicator

As would be expected, the pH of the solution has a pronounced effect upon the manner in which the indicator functions⁸. In the presence of so much alcohol, the pH value will of course be apparent rather than real¹⁰. The best pH range is from 3.0 to 4.0 and the distinctness of end-point increases with increasing volume of indicator (from 0.1 to 0.3 ml) and then diminishes with larger indicator volumes (from 0.3 to 0.4 ml). These indicator volumes are based on a 25 ml aqueous portion of the solution to be titrated.

RESULTS

Samples of the twelve coals were analysed in triplicate by the modified oxygen-flask method using Arsenazo (III) as titration indicator and by the Eschka (ASTM) method. In the former method, the end-point was approached by both direct and back titration. It will be seen in *Table 2* that the maximum deviation in values shown by direct titration was generally greater than by back titration. Although the maximum deviation of back titration was generally greater than that of Eschka determination, the deviation was well within that allowable for Eschka values according to ASTM standards¹⁵. The number of digits retained in the sulphur values in *Table 2* is intended to show the trends of their differences rather than to claim unusual precision.

Since the samples chosen included some with both high and low sulphur and ash, it is of interest to note that there seems to be no obvious correlation between the differences in the Eschka and oxygen-flask values (shown as A–C in *Table 2*) and the amounts of sulphur and ash. It would appear then that the presence of ash does not, in the oxygen-flask method, affect the conversion of sulphur to sulphur-oxide gases in the sample.

CONCLUSIONS

The oxygen-flask method modified by using Chromel 'A' wire for the combustion-grate material rather than platinum

Table 2 Determination of total sulphur in Canadian coals. Comparison of modified oxygen-flask and Eschka values

Sample No.	Ash (%)	Total sulphur (% dry basis)							
		Eschka method		Oxygen-flask method				Difference (Eschka method - oxygen-flask method)	
		Mean 'A'	Max. deviation	Direct titration with Ba(ClO ₄) ₂		Back titration with H ₂ SO ₄		(A-B)	(A-C)
		Mean 'B'	Max. deviation	Mean 'C'	Max. deviation				
1	6.8	3.379	0.004	3.260	0.070	3.340	0.022	+0.080	+0.034
		3.383		3.330		3.338			
		3.380		3.310		3.346			
2	24.5	2.323	0.024	2.257	0.081	2.340	0.025	+0.039	+0.009
		2.347		2.301		2.330			
		2.340		2.338		2.328			
3	17.1	0.968	0.047	0.970	0.037	1.000	0.020	+0.022	+0.001
		1.015		0.987		0.991			
		0.991		0.950		0.990			
4	12.0	0.316	0.001	0.262	0.038	0.331	0.036	+0.035	+0.007
		0.317		0.281		0.295			
		0.316		0.300		0.309			
5	10.1	0.522	0.016	0.468	0.042	0.530	0.043	+0.037	+0.007
		0.538		0.497		0.497			
		0.526		0.510		0.522			
6	8.6	0.482	0.024	0.457	0.040	0.471	0.013	+0.002	+0.005
		0.475		0.497		0.458			
		0.458		0.457		0.467			
7	14.0	0.937	0.004	0.954	0.035	0.951	0.011	-0.003	-0.008
		0.941		0.919		0.940			
		0.938		0.953		0.947			
8	9.3	0.744	0.015	0.679	0.024	0.712	0.025	+0.045	+0.020
		0.729		0.703		0.705			
		0.735		0.690		0.716			
9	8.1	0.472	0.014	0.482	0.022	0.470	0.011	-0.006	-0.008
		0.471		0.477		0.481			
		0.458		0.460		0.475			
10	19.6	1.333	0.027	1.316	0.028	1.331	0.021	+0.015	+0.020
		1.360		1.344		1.331			
		1.340		1.327		1.324			
11	12.2	0.507	0.011	0.514	0.027	0.514	0.014	+0.006	+0.001
		0.512		0.487		0.503			
		0.501		0.503		0.506			
12	11.7	0.273	0.015	0.290	0.028	0.285	0.005	-0.004	-0.007
		0.284		0.262		0.280			
		0.269		0.284		0.282			

and using Arsenazo (III) rather than Thorin as indicator is evidently applicable to total-sulphur analysis of coals of widely varying amounts of sulphur and ash. The method is particularly suitable for small numbers of samples and for control purposes in which results can be obtained quickly and by relatively untrained analysts especially if the back titration approach to the end-point is used. The precision appears to be similar to that obtained by the Eschka method by analysts in the same laboratory¹⁵.

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APPENDIX I

Reagents

(All reagents of analytical grade and the water, distilled).

Arsenazo (III), 0.050% (w/v): 50 mg of Arsenazo (III) (J. T. Baker Co.) was dissolved in 100 ml of water.

Barium perchlorate, (0.01 N): 3.9 g of barium perchlorate, $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (G. F. Smith Co.) was dissolved in 400 ml of water, diluted to 2 litres with isopropyl alcohol and the pH adjusted to 3.5 with a few drops of 7% (v/v) perchloric acid.

Ion exchange resin: Dowex 50-X8 cation exchange resin (J. T. Baker Co.) in the H-ion condition, 50 to 100-mesh.

Procedure

Weigh from 50 to 150 mg of minus 60-mesh coal onto a flag-shaped piece of Whatman No.42 filter paper, tail in the upper right hand corner (2 in. square with a 1 in. by $\frac{1}{8}$ in. tail). Fold the filter paper incorporating the coal up from the bottom twice. Roll from the left into a small cylinder and insert in wire grate with the tail upright for ignition. Add 15 ml of 5% hydrogen peroxide solution to the flask and flush with oxygen at 15 l/min for 60 to 70 s. Ignite the filter paper, stopper the flask firmly and seal with water. When combustion is complete (in about 90 s) shake the flask vigorously for 2 min and allow it to stand for about 30 min. Rinse the stopper, sample holder and flask with about 35 ml of water and add the washings to the combustion solution. Pass the total solution through an ion exchanger (resin depth: 12 cm in a glass tube 30 X 1.2 cm excluding stopcock) at a rate of 6 ml/min and wash through with 50 ml of water in several portions. Cover the resin bed each time with water to a height of 1 cm. Take a 25 ml aliquot of the effluent, 100 ml of isopropyl alcohol and 0.3 ml of Arsenazo (III), add excess of 0.01 barium perchlorate (about 5 ml more than required for direct titration) and back titrate with 0.01 N sulphuric acid until the blue colour turns to rose.

Calculation for back titration procedure

$$S = 16.03((V_1 \times F) - V_2)/W$$

where

- S = percentage of total sulphur in the sample
 V_1 = volume of 0.01 N barium perchlorate (ml)
 V_2 = volume of 0.01 N sulphuric acid (ml)
 F = normality factor of 0.01 N barium perchlorate against 0.01 N sulphuric acid
 W = weight of sample (mg)

APPENDIX II

Jig for making wire combustion grates for oxygen-flask analyses*

The jig shown in Figure 2 is made of Keewatin hardened (R^c 58) steel. The mandrel is held in place in the 'L' shaped stationary block (a) by the retaining pin (c). A longitudinal slot in the mandrel extending from the threaded portion through the handle serves to anchor the top of the grate during the winding process.

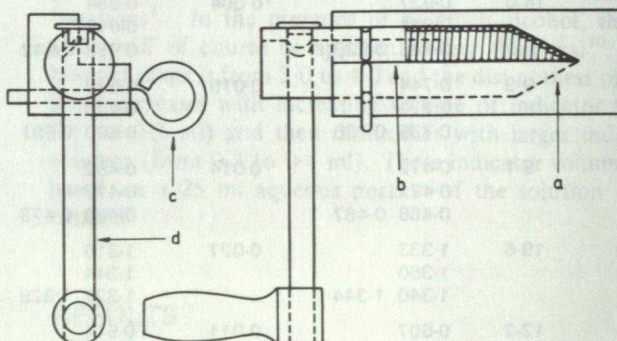


Figure 2 Jig for making wire combustion grates for oxygen-flask apparatus

In winding a grate, block (a) of the jig is clamped in a small bench-vice and 18 gauge wire laid in the longitudinal slot of the screw, with one end of the wire projecting about 25 mm past the handle. The crank handle (d), is turned in a clockwise direction and the wire fed under tension into the cylindrical screw thread until the wire reaches the apex of the cone. It is then automatically cut leaving a finished end on the cone.

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