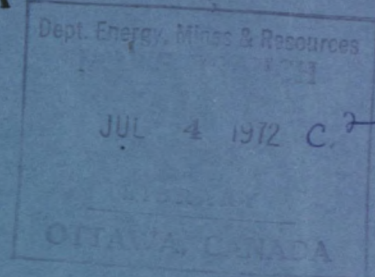




CANADA

DEPARTMENT OF  
ENERGY, MINES AND RESOURCES  
MINES BRANCH  
OTTAWA



*THE USE OF ARSENAZO(III) IN  
THE DETERMINATION OF TOTAL SULPHUR  
IN COAL BY THE OXYGEN-FLASK METHOD*

S. M. AHMED AND B. J. P. WHALLEY

FUELS RESEARCH CENTRE

Reprinted from FUEL - THE JOURNAL OF FUEL SCIENCE,

Vol. 48, 1969, No. 2, pps 217-219

Reprint Series RS 111

Price 25 cents

CONCENTRATION FACTORS

© Crown Copyrights reserved

Available by mail from Information Canada, Ottawa,  
and at the following Information Canada bookshops:

HALIFAX  
1735 Barrington Street

MONTREAL  
1182 St. Catherine Street West

OTTAWA  
171 Slater Street

TORONTO  
221 Yonge Street

WINNIPEG  
393 Portage Avenue

VANCOUVER  
657 Granville Street

or through your bookseller

Price: 25 cents Catalogue No. M 38-8/111

Price subject to change without notice

Information Canada  
Ottawa, 1972

## The Use of Arsenazo(III) in the Determination of Total Sulphur in Coal by the Oxygen-flask Method

THE oxygen-flask method<sup>1</sup> for determining sulphur in organic compounds has been used for several years. It has also been applied to the determination of total sulphur in coals by the B.C.R.A.<sup>2</sup> and by D. B. RATCLIFFE and A. T. S. CUNNINGHAM<sup>3</sup> using Thorin as titration indicator. Despite the simplicity of the apparatus and technique, the method has not been widely adopted for coals partly because it has lacked an indicator displaying a sharp colour contrast at the end-point, thus restricting its use to experienced analysts. Recently S. B. SAVVIN *et al.*<sup>4</sup>, and K. HOZUMI and K. UMEMOTO<sup>5</sup> have pointed out that a new indicator Arsenazo(III) gives a much more definite end-point than Thorin when used in analysing essentially pure organic compounds for sulphur content. Moreover the end-point is a reversible one.

A. M. G. MACDONALD<sup>6</sup> considered metals other than platinum unsatisfactory as sample holders and catalysts for the combustion of organic compounds, but recently A. R. JOHNSON JR and G. B. MCVICKER<sup>7</sup> claimed that Chromel 'A' provided better combustion than platinum for inorganic sulphides and was much more durable under vigorous combustion conditions. The object of this note is to report the results of preliminary investigations we have made to adapt the oxygen-flask method for the determination of total sulphur in coals by the use of Arsenazo(III) as the titration indicator and Chromel 'A' as sample holder.

The method used was as follows. The combustion apparatus consisted of a 2-litre Pyrex Erlenmeyer flask from which was suspended from a Neoprene stopper by a piece of 16-gauge Chromel 'A' wire, a spiral sample holder wound from 18-gauge Chromel 'A' wire. About 150 mg of minus 60-mesh coal was accurately weighed on to a flag-shaped piece of Whatman No. 42 filter paper measuring 2 in. square with a 1 in. by  $\frac{1}{8}$  in. tail. The paper containing the coal was carefully formed into a small roll and fitted into the sample holder with the tail projecting upwards. Fifteen millilitres of five per cent hydrogen peroxide solution was added to the flask. The flask was flushed with oxygen; the sample was introduced into the flask, the tail of filter paper ignited and the stopper inserted. Combustion was complete in about 40 to 60 seconds depending on the nature of coal. The flask was then shaken vigorously and kept standing for about 30 minutes or until the

\*Eschke method was used as a reference technique. Determinations were made in a different laboratory.

cloud of gas-borne combustion products had disappeared. The stopper, sample holder and flask were rinsed with about 15 ml of distilled water which was added to the solution of combustion products. Although titration in the presence of Thorin of combustion solutions of some coals analysed in this laboratory did not require removal of interfering ions (as was also noted by the B.C.R.A.<sup>2</sup> and by Ratcliffe and Cunningham<sup>3</sup>) the same solutions could not be titrated using Arsenazo(III) without using ion exchange because of an unsatisfactory end-point. Consequently to permit a comparison of the relative effectiveness of the two indicators, a solution of combustion products was passed through a cation-exchange column (Dowex 50W-X8) in the hydrogen-ion condition at a rate of 6 ml/min. The column was then washed with 20 to 25 ml of distilled water in such a way that the liquid level did not drop to less than 1 cm above the top of the resin before water was added. The apparent pH of the solution after passing through the column and after the addition of alcohol was found to be between 2.5 and 4.0. The effluent from the column was transferred directly to a 50 ml volumetric flask and diluted to the mark. This will be referred to as solution 'A'.

To compare the Thorin and Arsenazo(III) indicators, the following procedure was used. A 25 ml aliquot of solution 'A' was pipetted into a 250 ml beaker, to which was added 100 ml of isopropyl alcohol, 0.3 ml of 0.2 per cent aqueous Thorin solution and one or two drops of 0.01 per cent aqueous methylene blue. To the remaining 25 ml of solution 'A', 100 ml of isopropyl alcohol and 0.3 ml of 0.05 per cent aqueous Arsenazo(III) solution were added. These concentrations of alcohol and indicator had been predetermined from a series of experiments to define optimum conditions for the end-point with the detailed results of experiments to be reported later. Both

Table 1. Determination of total sulphur in coal using oxygen-flask method: Comparison of values between Thorin and Arsenazo(III) indicators

Rank of coal	High-volatile 'A' bituminous Canadian coal				High-volatile 'A' bituminous American coal			
Ash, %	5.95				5.04			
	Total sulphur, %				Total sulphur, %			
Method	Eschka*	Oxygen-flask			Eschka*	Oxygen-flask		
		Thorin (A)	Arsenazo(III) (B)	Diff. (A-B)		Thorin (A)	Arsenazo(III) (B)	Diff. (A-B)
	1.43	1.410	1.423	-0.013	0.69	0.723	0.733	-0.010
	1.43	1.380	1.380	0.000	0.69	0.743	0.726	+0.017
	1.40	1.400	1.410	-0.010	0.69	0.739	0.722	+0.017
	1.44	1.370	1.370	0.000	0.66	0.743	0.722	+0.021
	1.40	1.374	1.374	0.000	0.67	0.743	0.722	+0.021
	1.47	1.400	1.410	-0.010	0.70	0.728	0.748	-0.020
	1.42	1.391	1.390	+0.001	0.66	0.759	0.759	0.000
	1.41	1.384	1.394	-0.010	0.65	0.765	0.753	+0.012
	1.41	1.430	1.400	+0.030	0.66	0.738	0.728	+0.010
	1.41	1.430	1.410	+0.020	0.71	0.703	0.687	+0.016
	1.41	1.410	1.387	+0.023	0.70	0.769	0.759	+0.010
	1.41	1.375	1.390	-0.015	0.70	0.753	0.769	-0.016
Max. value	1.47	1.430	1.423	+0.030	0.71	0.769	0.769	+0.021
Min. value	1.40	1.370	1.370	-0.015	0.65	0.703	0.687	-0.020
Range	0.07	0.060	0.053	0.045	0.06	0.066	0.082	0.041
Arithmetic mean	1.42	1.396	1.394	+0.001	0.68	0.742	0.735	+0.007
Standard deviation	0.019	0.020	0.016	0.013	0.020	0.018	0.022	0.009

\*Eschka method was used as a referee technique. Determinations were made in a different laboratory.

portions of solution 'A' were separately titrated with 0.01N alcoholic barium perchlorate solution using 5- or 10-ml micro-burettes with 0.01- and 0.02-ml subdivisions respectively. The colour changes were from yellow to pale pink for Thorin and rose to blue for Arsenazo(III). Blank determinations were made in the usual way and titre values corrected. A series of twelve individual combustions was made on samples of two high-volatile 'A' bituminous coals: one Canadian and one American, containing 1.42 and 0.68 per cent sulphur, and 5.95 and 5.04 per cent ash respectively. The Eschka determinations were made in another laboratory in the Fuels Research Centre. *Table 1* shows that the variations between the Thorin and Arsenazo(III) determinations for individual samples were much smaller than the variations between samples. This indicates that the larger variations between samples were due to errors introduced into the analysis before titration. That the individual values of both Thorin and Arsenazo(III) agree fairly closely would appear to indicate no advantage to using Arsenazo(III). However, when the two types of titration were performed by unskilled operators the Thorin values became quite erratic and unreliable, whereas the Arsenazo(III) values were acceptable and were obtained without difficulty. It will be seen that the values of both Thorin and Arsenazo(III) titrations agree within acceptable variation with the Eschka values according to A.S.T.M. specifications<sup>8</sup>.

The main advantage of using Arsenazo(III) in the determination of total sulphur by the oxygen-flask method is that it can be substituted for Thorin with no loss of accuracy, but with a considerable gain in facility in titration. The use of Chromel 'A' as support material for the sample during combustion appears to be as satisfactory as platinum wire.

To determine the general applicability of the method, it will be necessary to do a considerable number of analyses involving a wide variety of coals of different rank and of different mineral matter, and this work is now in progress.

S. M. AHMED  
B. J. P. WHALLEY

*Fuels Research Centre, Mines Branch,  
Department of Energy, Mines and Resources,  
Ottawa, Ontario, Canada*

(Received February 1969)

## REFERENCES

- <sup>1</sup> SCHONIGER, W. *Mikrochim. Acta*, 1956, 869-876
- <sup>2</sup> *Coke Res. Rep. No. 13*, November 1961, 'An examination of novel methods for the determination of sulphur in solid fuels'. British Coke Research Association: Chesterfield, Derbyshire
- <sup>3</sup> RATCLIFFE, D. B. and CUNNINGHAM, A. T. S. *Fuel, Lond.* 1968, 47, 89-92
- <sup>4</sup> SAVVIN, S. B., DEDKOV, Y. M. and MAKAROVA, Y. P. *Zh. analyt. Khim., Mosk.* 1962, 17, 43-47
- <sup>5</sup> HOZUMI, K. and UMEMOTO, K. *Microchem. J.* 1967, 12, 46-54
- <sup>6</sup> MACDONALD, A. M. G. *Analyst*, 1961, 86, 3-12
- <sup>7</sup> JOHNSON JR, A. R. and McVICKER, G. B. *Analyt. Chem.* 1966, 38, 913-915
- <sup>8</sup> *A.S.T.M. Stand.* 1966, part 19