A MODIFICATION OF MOTT'S METHOD FOR THE DETERMINATION OF PYRITIC SULFUR IN COAL

by

Willem van Hees and Edward Early

Research Department
Baltimore Gas and Electric Company
Baltimore, Maryland

Abstract

Mott's method, involving two simultaneous acid extractions of powdered coal samples, has been simplified to a labor saving non-simultaneous extraction procedure, applicable in cases where only pyritic sulfur has to be determined.

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Introduction

Mott[2] developed a procedure for the determination of sulfate and pyritic sulfur in coal, that is referred to in the literature as the British Coke Research Association method. It differs from the Powell and Parr[4] method in that the extractions take place with dilute boiling acids during one half hour, instead of at room temperature, or at 60°C, for periods up to forty hours. Mott's method is recommended by Edwards, Daybell and Pringle[1] when the highest accuracy is required. A short description follows.

Five grams of coal, ground to pass a No. 70 sieve, are boiled for one half hour with 50 ml of 5 N HCl in a 500 ml conical flask provided with a reflux condenser. The coal residue is then filtered off and washed. In the combined filtrate and washings, iron and, if desired, the sulfate sulfur are determined.

One gram of the same coal powder is boiled for one half hour with 50 ml of 2 N HNO_3 in the manner indicated above. After filtering and washing the residue, iron is determined in the combined filtrate and washings. The percentage iron found by hydrochloric acid extraction (Fe') is subtracted from the percentage found by nitric acid digestion (Fe"). The former is non-pyritic in origin, while the latter is pyritic as well as non-pyritic. The concentration of pyritic sulfur is calculated from the proportion, S = 1.148(Fe"-Fe').

In case it is not necessary or essential to determine sulfate, but only pyritic sulfur, a simplification resulting in the saving of work, can be applied.

It is proposed that, in contrast to the B.C.R.A. or "simultaneous" method, a "non-simultaneous" procedure be followed. The coal is extracted with HCl, filtered and washed. The extract is discarded. The residue is quantitatively transferred to the nitric acid, extracted, filtered and washed. The iron in the combined filtrate and washings is determined; it is solely of pyritic origin. The pyritic sulfur is then calculated from the proportion, S = 1.148 Fe.

Both methods were applied to a series of samples of bituminous coals from Pennsylvania and West Virginia.

Experimental

Determinations of pyritic sulfur were made in all samples by the B.C.R.A. method. These were followed by determinations made by the modified method according to the following detailed description.

One gram of coal, powdered to pass a No. 70 sieve (American Society for Testing Materials, E 11-39) is boiled for one half hour in a 500 ml conical flask with 50 ml of 5 N HCl. The flask is provided with a reflux condenser.*

The coal is filtered off and washed with dilute HCl (1:20) until the filtrate is free of iron (test with KCNS), then a few times with distilled water. The filtrate is discarded.** Filter paper and residue are then transferred to a 500 ml conical flask and boiled for one half hour with 50 ml of 2 N HNO_3 in the manner indicated above. The contents of the flask are filtered and repeatedly washed with 2 N HNO_3. The iron in the combined filtrate and washings is determined in one of the usual ways. The procedure used in this work, a titration of Fe^{++} with Ce^{++++}, is given in detail in standard texts(3,5).

Table I gives data obtained with Mott's method (Column A), and with the proposed modification (Column B), for the pyritic sulfur contents, for twelve samples of pulverized coal.

TABLE I

Pyritic Sulfur Content, Percent of Coal

Coal	A B.C.R.A. Method	B Modified Method
1	.94	.97
2	1.22	1.22
3	.81	.81
4	.95	1.02
5	.65	.63
6	2.23	2.33
7	.88	.87
8	.28	.27
9	.91	.93
10	1.53	1.48
11	.94	.94
12	.88	.87

Discussion of Results

It was found that it was difficult in some cases (particularly in the case of coals with a high pyritic sulfur content) to prepare duplicate samples. Very careful mixing of the samples of powdered coals resulted in the values tabulated. It is likely that the cause of erroneous results was in the inhomogeneous distribution of the larger pyrite particles in the ground coal. It has been shown that these particles are present associated with only a small amount of organic matter(6). Since they are considerably denser than the organic material in coal, it seems quite possible that pyrite particles may become locally concentrated in the grinding process and during transport and subsequent handling. The often considerable inhomogeneity of coal in its natural state is an additional potential source of sampling difficulties.

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* The use of rubber stoppers (a potential source of sulfur) in acid extraction apparatus is permissible, because only iron is determined.

** No attempt to determine sulfate in this filtrate should be made since only one gram of coal was used. A five gram sample, as recommended by Mott(2) for sulphate sulfur determinations, is advisable.

The tabulated results are averages of duplicate determinations. An additional ninety-six pairs of duplicate determinations of pyritic sulfur were made by the modified method, using samples of coal from as many different sources. These data are not presented, however, they were used in the statistical calculations.

The standard deviation of the differences between duplicate pairs of determinations was found to be equal to ± .087% pyr. S for Mott's method (based on twelve sets of data), and equal to ± .054% pyr. S for the modified method (based on ninety-six sets of data).

In the case of Mott's method, the expected uncertainty in the mean of a pair of duplicate determinations, will not exceed ± .192% pyr. S in 95% of all cases. At the same confidence level, the expected uncertainty in the mean of a pair of duplicate determinations will not exceed ± .106% pyr. S for the modified method. On the basis of these calculated values, it may be concluded that the modified method affords greater precision than Mott's method. The modified method is simpler (readings and observations are reduced to 50% of the number necessary for Mott's method). This may in part account for the greater precision of the modified method.

Application of Student's t test to the data in Table I shows that there is no significant difference between the mean values obtained for the series of twelve samples by the two methods. Therefore, it may be concluded that there is no significant systematic difference between the two methods.

Conclusion

A modification of Mott's method for the determination of pyritic sulfur in coal was developed. This modification is labor saving. Statistical treatment of data obtained on a series of coal samples, using both methods, shows that the modified method compares favorably with the existing method.

References

1 Edwards, A. H., Daybell, G. N., Pringle, W. J. S., Fuel 37, 47 (1958)

2 Mott, R. A., Fuel 29, 53 (1950)

3 Pierce, W. C., and Haenisch, E. L., "Quantitative Analysis," Chapter XII, New York (1937)

4 Powell, A. R., and Parr, S. W., U. of Ill. Bull. No. 111, 62 (1919)

5 Treadwell, F. P., and Hall, W. T., "Analytical Chemistry," Vol. II, pp 54 and 637, New York (1942)

6 van Hees, W., "The Separability of Pyrites Particles in Some Pulverized Coals." Presented before the Division of Gas and Fuel Chemistry, A.C.S., Chicago, Ill., Meeting, Sept. 7-12, 1958