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FUEL RESEARCH INSTITUTE

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TECHNICAL

NO. 11 OF 1974

A MODIFIED METHOD OF ANALYSIS FOR CALCIUM, MAGNESIUM, POTASSIUM AND SODIUM IN COAL ASH

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INTRODUCTION

In the routine analysis of coal ash at the Fuel Research Institute, the determination of calcium and magnesium is done by an atomic absorption technique, and the determination of sodium and potassium is carried out using a flame emission technique. Two solutions are thus prepared from the ash sample, one for calcium and magnesium and a different one for sodium and potassium.

To save time and labour when many samples have to be analysed, an attempt was made to find a method of preparing a single solution which could be used for the analysis of all four constituents.

PREPARATION OF SOLUTIONS - METHODS USED AT PRESENT

A. POTASSIUM AND SODIUM

Coal ash is heated with sulphuric acid and hydrofluoric acid, the dry residue is heated over a flame until fuming ceases, and the final residue is dissolved in hydrochloric acid. This solution, after the addition of phosphoric acid, is then made up to 100 cm^3 with distilled water in a volumetric flask.

B. CALCIUM AND MAGNESIUM

Coal ash is heated with nitric acid and hydrofluoric acid and the dry residue is dissolved in hydrochloric acid. This solution is then made up to 100 cm^3 with distilled water in a volumetric flask.

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For some time the determination of the four constituents has been done by using solution A with emission spectroscopy for potassium and sodium, and solution B with atomic absorption spectroscopy for calcium and magnesium.

With most samples, method B results in a more satisfactory solution in that the solution is clear and colourless and does not have to be filtered.

When solution B was used to determine potassium and sodium, however, it was found that very high apparent sodium values were obtained. Potassium values were only slightly higher than when the correct solution (i.e. A) was used.

As a first step, method B was modified by adding phosphoric acid to the hydrochloric acid solution before the final dilution to 100 cm^3, thus bringing this solution into line with solution A.

Alkali determinations were then carried out on these solutions. The results are shown in Table 1.

TABLE 1

COMPARISON OF SOLUTIONS PREPARED BY METHODS A AND B

Sample No.	Solution prepared by	% Na_2O	% K_2O
73/103E	Method A	2,12	1,00
73/103F	(Standard alkali method)	0,89	2,75
73/103E	Method B	3,35	1,13
73/103F	(+ phosphoric acid)	1,55	2,81

From this test it appears that there is a fair agreement between potassium results, but that the sodium results from method B are still too high.

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The effect of adding further amounts of phosphoric acid was determined by using the solution from one of the above samples (73/103F) and testing for sodium only. The results are shown in Table 2.

TABLE 2

THE EFFECT OF ADDING FURTHER AMOUNTS OF PHOSPHORIC ACID

Sample No.	Volume of solution used (cm^3)	Additional phosphoric acid solution added (cm^3)	% Na_2O
73/103F	10	0,2	1,55
Solution prepared	10	0,4	1,55
by Method B with	10	0,6	1,55
the addition of	10	0,8	1,55
phosphoric acid	10	1,0	1,55

(N.B. Phosphoric acid solution: 20 cm^3 H_3PO_4 (d = 1,7 g/cm^3) made up to 1 000 cm^3 with distilled water.)

From this test it appears that additional amounts of phosphoric acid have no effect on the apparent sodium content.

The essential difference between method A and method B (phosphoric acid added), is that the residue in method A contains the constituents of the ash in sulphate form whereas the residue in method B contains the constituents in nitrate form. Consequently the following modification was made to method B.

Approximately 10 drops of 50% sulphuric acid were added to the dry residue in the platinum crucible and this was then heated carefully over a flame until fuming ceased. The new residue was then dissolved

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in hydrochloric acid and this solution, after the addition of phosphoric acid, was made up to 100 cm^3 with distilled water.

Alkali, calcium and magnesium determinations were then carried out on solutions A, B and B(modified), prepared from sample 73/103F.

The results are shown in Table 3.

TABLE 3

COMPARISON OF SOLUTIONS PREPARED BY METHODS A, B AND B (MODIFIED)

Solution prepared by:	% Na_2O	% K_2O	% CaO	% M_9O
Method A (standard alkali method)	2,10	1,00	12,0	3,00
Method B (+ phosphoric acid)	3,00	1,12	12,6	3,15
Method B (modified by addition of sulphuric acid)	2,12	1,00	12,0	3,00

From Table 3 it appears that method B (modified) yields alkali results comparable to method A (assumed to be correct), while all three methods give good results for calcium and magnesium.

As a further test, six coal ash samples were taken and analysed for alkalis, calcium and magnesium, using methods A and B (modified).

The results are shown in Table 4.

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TABLE 4

COMPARISON OF SOLUTIONS PREPARED BY METHODS A AND B (MODIFIED) FROM SIX DIFFERENT ASH SAMPLES

Sample	Solutions prepared by:	% Na_2O	% K_2O	% CaO	% MgO
1	Method A	1,71	0,55	7,1	2,28
2		0,33	0,85	2,3	0,90
3		0,21	0,46	8,4	1,96
4		0,39	0,90	10,1	2,88
5		0,55	0,46	6,9	2,55
6		1,15	1,84	1,9	2,15
1	Method B (modified)	1,71	0,55	7,1	2,28
2		0,33	0,85	2,3	0,90
3		0,21	0,46	8,2	1,96
4		0,39	0,90	10,0	2,88
5		0,55	0,46	6,9	2,55
6		1,15	1,84	1,9	2,15

The results of the analyses shown in Table 4 show clearly that solutions prepared by either method A (the standard method for alkalis) or method B (modified) may be used for the determination of the alkalis as well as calcium and magnesium. It is therefore possible to determine these four constituents of a coal ash by preparing a single solution for each sample.

It may be worth mentioning that the agreement between the two methods is surprisingly good. Analyses done at different times, even by the same method of solution preparation, do not always agree so well.

(SIGNED) J.F. HARRIS

SENIOR RESEARCH OFFICER

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APPENDIX

PREPARATION OF SOLUTIONS - DETAILED INSTRUCTIONS

Weigh 0,200 g of coal ash (previously heated at 800°C for 20 minutes and then cooled in a desiccator)into a platinum crucible.

Method A

Add 10 drops of 50% sulphuric acid and 5 cm^3 hydrofluoric acid to the ash. Heat on a sandbath until a dry residue is obtained. Repeat this procedure. Then heat carefully over a flame until fuming ceases.

Method B

Add 5 cm^3 concentrated nitric acid and 5 cm^3 hydrofluoric acid to the ash. Heat on a sandbath until a dry residue is obtained. Repeat this procedure. Then add 2 cm^3 nitric acid and heat again to dryness. Allow to cool, add 10 drops of 50% sulphuric acid and heat carefully over a flame until fuming ceases.

Dissolve the residue (from A or B) in 10 cm^3 4N hydrochloric acid, add 5 cm^3 phosphoric acid solution and make up to 100 cm^3 in a volumetric flask.

Reagents

Nitric acid,	55%
Hydrofluoric acid,	48%
Sulphuric acid,	d=1,84
Phosphoric acid solution:	
20 cm^3 H_3PO_4 (d = 1,7 g/cm^3) diluted to 1 000 cm^3.	
Hydrochloric acid,	4N

/Literature .....

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