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THE FLAME PHOTOMETRIC DETERMINATION OF SODIUM, POTASSIUM, MAGNESIUM AND IRON OXIDES IN PORTLAND CEMENT

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ABSTRACT

A method is presented for the simultaneous flame photometric determination of sodium, potassium, magnesium and iron oxides in portland cements. The instrument used is a Beckman DU spectrophotometer with flame and photomultiplier attachments and laboratory constructed recorder. No chemical separations are necessary and all determinations are done on the same sample solution. Good concordance of results was obtained for 17 samples analyzed by photometric and gravimetric methods. This study showed that the determination of sodium, potassium, magnesium and iron oxides by flame photometry is feasible and results in a considerable saving of time and effort.

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For many years the Michigan State Highway Department has required a chemical analysis of portland cement used in state highway construction, the determination of sodium, potassium, magnesium and iron oxides being made by the standard chemical methods of the American Society for Testing Materials. These methods are laborious, time consuming, and the personnel must be well trained to perform the meticulous operations. Therefore, flame photometric methods for determining these constituents were investigated in an effort to save time and conserve the work of trained analysts.

Eubank and Bogue (1) worked out a method of utilizing flame photometry in the alkali metal determinations in portland cements, and Diamond and Bean (2) later modified the work, making it applicable to a different type of flame photometer.

Pritchard, Bogue and Bean were placed on the working committee on methods of chemical analysis of portland cement of the ASTM, and prepared tentative specifications for the determination of sodium and potassium oxides by flame photometry. Their proposed method was adopted by the Society as C-228-49T, and later combined with tentative method C-114-51T, of Part 3, 1955 ASTM Standards. Pritchard (3) in conjunction with this committee has since been working in tentative specifications for magnesium oxide determination in portland cement.

It was thought that, by using the standard solutions worked out by Eubank and Bogue (1) and simply adding known amounts of magnesium and iron,

this established method could be extended to include these elements without otherwise altering the method. At the same time, it was felt that the standards, since they would more accurately represent a cement sample, would give rise to even less interference than may be encountered in the ones containing only sodium, potassium and calcium.

Experimental

This study was made with a Beckman DU, with a model 9200 flame attachment equipped with an oxyhydrogen aspirator burner and a model 4300 photomultiplier attachment. The flame photometer was modified for use as a recording instrument by following the instructions of King and Priestly (4). This made it possible to obtain a continuous record of the photometric response with time, thereby eliminating the human error in averaging a fluctuating meter. It is, of course, not necessary to adjust the absorption dial, thereby saving time in individual readings. Another advantage inherent in this method of recording is that any change in operating conditions affecting the flame is immediately apparent on the continuous record. A photograph of the complete apparatus is shown in Figure 1.

All water used was distilled and allowed to remain over a demineralizing resin until used. All glassware was "Pyrex" or Kimbal "Normax" brand, and all storage containers were of polyethylene. All reagents met American Chemical Society specifications.

Instrument settings are shown in Table 1. In each case, the oxygen pressure was 11 pounds, and hydrogen 4 pounds.

TABLE 1
INSTRUMENT SETTINGS

Element	Wave Length, mu	Photomultiplier Sensitivity	Slit Width mm
Sodium	589	2	0.03
Potassium	768	Full	0.10
Magnesium	383	Full	0.11
Iron	386	Full	0.11

For convenience sake, a blue tube was used in the circuit exclusively. In the case of potassium, this accounts for the high sensitivity setting. It is noted that in the case of magnesium and iron, with the sensitivity set at full, narrow slit widths of approximately .1 mm are possible, thereby leading to readings with a minimum of interference. Since magnesium interferes with iron (because of its close proximity), the 386 mu setting for iron should be at the long wavelength end. The sodium is here detected by the 589 mu line (emitted by the neutral sodium atom), potassium by the 768 mu line, magnesium by the 383 mu molecular band (emitted by the molecular magnesium oxide) and iron by the 386 mu line.

Calibration standards were prepared to contain each cation in different amounts, chosen to cover the expected concentration range, as in Table 2.

TABLE 2
COMPOSITION OF CALIBRATION STANDARDS

Standard No.	Proportions, parts per million				
	Na_2O	K_2O	MgO	Fe_2O_3	CaO
1	0	0	0	0	6300
2	10	10	150	150	6300
3	25	25	200	200	6300
4	50	50	250	250	6300
5	75	75	300	300	6300
6	100	100	350	350	6300

The preparation of the standards was as follows:

A stock solution containing the equivalent of 1000 ppm of sodium oxide was prepared by dissolving 1.8858 g of sodium chloride in water and diluting to 1 liter in a volumetric flask. 1.5830 g of potassium chloride was dissolved to make a liter of solution containing the equivalent of 1000 ppm of potassium oxide. A 3500 ppm solution of magnesium oxide was prepared by dissolving 3.5000 g of magnesium oxide in 50 ml of 6N HCl, and diluting to liter. A stock solution containing the equivalent of 3500 ppm of iron oxide was prepared by dissolving 2.4480 g of iron wire in 35 ml of 6N HCl and diluting to 1 liter. A lime acide solution containing 63,000 ppm of calcium oxide and 500 ml of HCl per liter was prepared by combining 300 ml of water and 112.5 g of calcium carbonate in a beaker, adding 500 ml of HCl, and diluting to 1 liter. The calcium oxide was necessary in the standards to compensate for interference from the large percentage of this oxide found in portland cement.

The standard solutions were prepared using the volume of stock solutions listed in Table 3:

TABLE 3
MAKEUP OF STANDARD SOLUTIONS

Standard No.	Volume of Stock Solutions					Diluted to Final Volume, ml
	Na_2O ml	K_2O ml	MgO ml	Fe_2O_3 ml	Lime-Acid ml	
1	0	0	0	0	100	1000
2	10	10	42.86	42.86	100	1000
3	25	25	57.14	57.14	100	1000
4	50	50	71.43	71.43	100	1000
5	75	75	85.71	85.71	100	1000
6	100	100	100	100	100	1000

If desired, these volumes could all be cut to one tenth, and the final solution diluted in a volumetric flask to 100 ml. The stock solutions were stored in tightly stoppered polyethylene bottles for future use.

The cement samples were prepared by dispersing 1.0000 g of cement in 25 ml of water, adding 5 ml 6N HCl, and diluting with 50 ml of water. All lumps were broken up with a glass rod, and the sample was digested for 15 minutes on a steam bath or hot plate. The sample was then filtered into a 100 ml volumetric flask, the beaker and paper washed with water, the solution cooled, diluted to 100 ml, and mixed thoroughly.

The instrument recorder is balanced at zero, with the shutter of the DU off, which compensates for any dark current. Standard No. 5 is placed in the flame and the correct wave length is located by rotating the wavelength dial and observing the point on this dial at which the largest amount of energy is recorded. To keep the record from going over the limits of the chart paper, the combination of sensitivity control on the recorder circuit, and slit width are adjusted so that standard No. 5 is recorded on the high end of the recorder chart. The rest of the standards, giving progressively less emission energy, will then be recorded stepwise toward the lower end of the chart. To check for flame fluctuations, one or two standards should be repeatedly run along with the cement samples over any long operating time, and the recorder sensitivity control adjusted to correct for any drift in the recorder reading.

Using the readings obtained from the six standard solutions, a calibration curve is made with recorder readings (relative emission values) as ordinate,

and ppm (or percentage) as abscissa. By superimposing the relative emission value of each oxide of the cement sample onto this calibration curve, the ppm, or percentage, may be read directly.

Results and Discussion

Seventeen portland cement samples, of different types, and their complete chemical analyses were obtained from the Testing Laboratory at Ann Arbor. An additional cement, Standard No. 177, was obtained from the National Bureau of Standards. The results of the chemical analysis and flame analysis of the oxides are shown and compared in Table 4, and the concordance of values for duplicate samples in Table 5. These results show that satisfactory concordance was obtained, both between methods and between duplicates by the same method.

As can be seen from the results, there is no regular variation between the two types of analyses, but further work in this or other laboratories will no doubt result in refinements in procedure and equipment, and so in reproducibility and accuracy.

A great saving in time is realized by this method over that of standard chemical methods, the eighteen reported analyses, along with standard solution preparation, being done in 24 working man-hours as opposed to approximately 100 man-hours required for the chemical method.

TABLE 4

RESULTS OF GRAVIMETRIC VS. FLAME PHOTOMETRIC ANALYSES

Sample No.	Na_2O, Percent			K_2O, Percent			MgO, Percent			Fe_2O_3, Percent		
	Grav.	Flame	Diff.	Grav.	Flame	Diff.	Grav.	Flame	Diff.	Grav.	Flame	Diff.
1	--	0.30	--	0.69	0.69	0	2.70	2.70	0	2.56	2.62	+0.06
2	--	0.29	--	0.57	0.58	+0.01	3.28	3.44	+0.16	2.50	2.92	+0.42
3	--	0.29	--	0.68	0.66	-0.02	2.34	2.22	-0.12	3.01	2.77	-0.24
4	--	0.16	--	0.98	0.97	-0.01	2.62	2.46	-0.16	2.29	2.36	+0.07
5	--	0.30	--	1.03	1.02	-0.01	3.10	2.97	-0.13	2.09	2.60	+0.51
6	0.25	0.26	+0.01	0.67	0.69	-0.02	2.32	2.18	-0.14	2.85	2.51	-0.34
7	0.34	0.34	0	1.04	1.02	-0.02	2.91	2.94	+0.03	2.41	2.44	+0.03
8	0.24	0.28	+0.04	0.79	0.80	+0.01	2.51	2.61	+0.10	2.73	2.55	-0.18
9	0.21	0.22	+0.01	0.66	0.67	+0.01	2.33	2.43	+0.10	2.96	2.56	-0.40
10	0.32	0.28	-0.04	0.57	0.62	+0.05	2.28	2.30	+0.02	2.75	3.01	+0.26
11	0.12	0.11	-0.01	0.12	0.13	+0.01	2.80	2.68	-0.12	1.81	1.93	+0.12
12	0.33	0.31	-0.02	0.58	0.56	-0.02	3.25	2.98	-0.27	2.56	2.50	-0.06
13	0.28	0.28	0	0.61	0.64	+0.03	2.50	2.66	+0.16	2.80	2.74	-0.06
14	0.15	0.18	+0.03	0.68	0.67	-0.01	2.96	2.86	-0.10	2.32	2.50	+0.18
15	0.27	0.30	+0.03	0.59	0.58	-0.01	2.43	2.50	+0.07	2.88	2.64	-0.24
16	0.18	0.17	-0.01	0.77	0.78	+0.01	1.97	2.22	+0.25	3.17	2.68	-0.49
17	0.18	0.18	0	0.44	0.44	0	3.43	3.76	+0.33	3.02	3.08	+0.06
Std. 177	0.14	0.15	+0.01	0.56	0.56	0	2.42	2.31	-0.10	2.38	2.30	-0.08

TABLE 5

CONCORDANCE OF
GRAVIMETRIC AND FLAME PHOTOMETRIC ANALYSES,
DUPLICATE SAMPLES

Sample No.	Deviation, Percent							
	Na_2O		K_2O		MgO		Fe_2O_3	
	Grav.	Flame	Grav.	Flame	Grav.	Flame	Grav.	Flame
1	- -	0.005	- -	0.010	0.055	0.035	0.040	0.015
2	- -	0.010	- -	0.005	0.035	0.080	0.020	0.005
3	- -	0.020	- -	0.010	0.075	0.005	0	0.010
4	- -	0.005	- -	0.020	0.025	0.125	0.020	0.025
5	- -	0.005	- -	0.010	0	0	0	0.035
6	- -	0.010	- -	0.020	0.080	0.035	0	0.040
7	- -	0	- -	0.005	0	0.065	0	0.110
8	- -	0.020	- -	0.010	0	0.050	0	0
9	- -	0.005	- -	0	0.010	0.030	0.005	0.045
10	- -	0.005	- -	0.005	0.025	0.020	0.010	0.070
11	- -	0.010	- -	0	0.055	0.020	0.020	0.030
12	- -	0.010	- -	0.010	0.010	0.055	0	0.015
13	- -	0.005	- -	0.005	0.015	0.065	0	0.025
14	- -	0.005	- -	0.010	0.010	0.035	0	0.015
15	- -	0	- -	0.005	0.010	0.065	0	0.040
16	- -	0.010	- -	0.005	0.010	0.040	0	0
17	- -	0	- -	0	0.010	0.020	0.015	0.080
Std. 177	- -	0	- -	0.005	-	0.030	-	0.020

REFERENCES

(1) Wm. R. Eubank and R. H. Bogue, "Studies on the Flame Photometer for the Determination of Na_2O and K_2O in Portland Cement", Paper No. 54 of the Portland Cement Association Fellowship at the National Bureau of Standards, August, 1949.

(2) J. J. Diamond and Leonard Bean, "Use of the Beckman and Perkin-Elmer Flame Photometers for the Determination of Alkalies in Portland Cement": Symposium on Flame Photometry, ASTM Special Technical Publication No. 116 .

(3) L. R. Pritchard, "Review of Flame Photometry," Working Committee on Methods of Chemical Analysis of Portland Cement, ASTM C-1.

(4) W. H. King, Jr., and Wm. Priestley, Jr., "A Modified Recording Flame Photometer," ASTM Special Technical Publication No. 116.

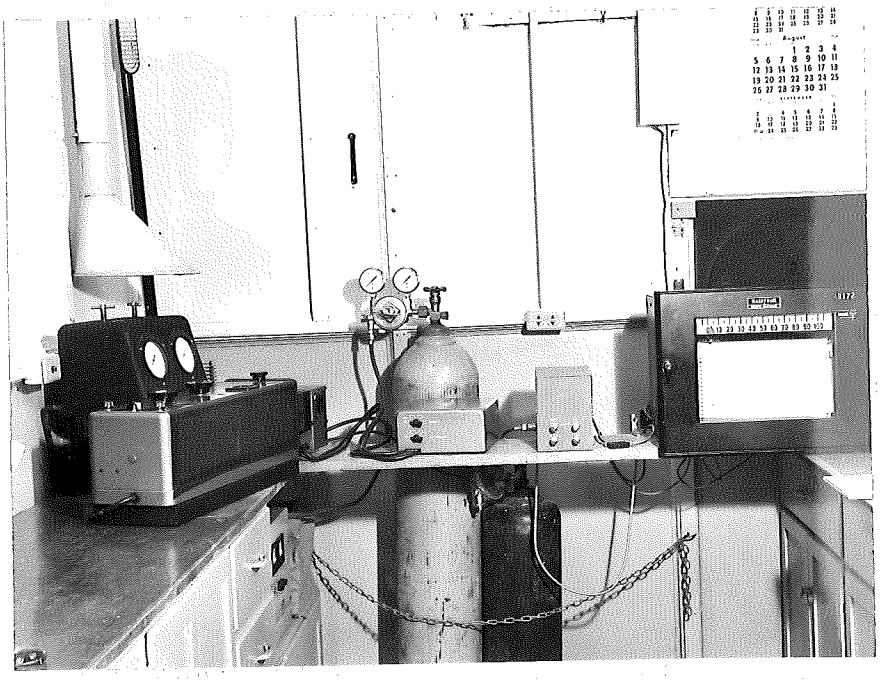

Figure 1. Recording Flame Photometer