

MICHIGAN  
STATE HIGHWAY DEPARTMENT  
JOHN C. MACKIE, COMMISSIONER

DETERMINATION OF  
SODIUM, POTASSIUM, MAGNESIUM AND IRON OXIDES  
IN PORTLAND CEMENT BY FLAME PHOTOMETRY

P. F. Biefeld  
C. C. Rhodes

LAST COPY  
DO NOT REMOVE FROM LIBRARY

Highway Research Project 56 B-37

Research Laboratory  
Office of Testing and Research  
Report No. 284  
March 3, 1958

## 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.

DETERMINATION OF  
SODIUM, POTASSIUM, MAGNESIUM AND IRON OXIDES  
IN PORTLAND CEMENT BY FLAME PHOTOMETRY

For many years determination of sodium, potassium, magnesium, and iron oxides in portland cement have been made in the Department's laboratories by standard chemical methods of the American Society for Testing Materials. These methods are laborious and time consuming, and require trained chemists for their proper performance. Therefore, flame photometric methods were investigated and techniques developed for determining these constituents rapidly and accurately. Determination of sodium and potassium oxides by flame photometry has been an established ASTM procedure since 1949, but the extension of this method to the determination of magnesium and iron oxides was accomplished in the Research Laboratory as part of a general program directed toward the application of spectroscopy to highway testing and research.

Seventeen portland cement samples and their complete chemical analyses were obtained from the Michigan State Highway Department Testing Laboratory at Ann Arbor. An additional cement, Standard No. 177, was obtained from the National Bureau of Standards for reference. Sodium, potassium, magnesium and iron oxides were determined on all these samples in the Research Laboratory by flame photometry. The analytical results from the two methods showed good concordance and demonstrated the feasibility of using flame photometry in the routine analysis of portland cement.

### Background

Essentially, a flame photometer is a device which atomizes a sample solution into a flame, isolates the characteristic spectral emission of an element, and detects and measures this emission. The new atomizer-burner units on the market can safely spray the most flammable samples, even gasoline, into the flame.

In inorganic mixtures, atoms and molecules are excited by application of energy in the form of heat or electricity. Low temperature excitation can best be obtained by a flame, producing temperatures from 1000 to 3000 deg C. Because of the low temperature of the flame in comparison to the arc and spark emission sources, it excites only the alkali metals (sodium, potassium, etc.), the lower states of the alkaline earths (calcium, magnesium, barium, etc.) and, to a lesser extent, other elements. This is an advantage when it is desired to detect these substances in the presence of a large amount of material of higher excitation potential.

It should be pointed out that the flame photometer does not yield direct results as gravimetric analysis does. All samples must be in liquid form

and their flame emission compared with that of a standard solution. For this reason, great care is necessary in preparing all solutions and, when determining elements in the few parts per million range, cleanliness is an absolute essential, even to the use of special sodium-free glassware.

The chief worry of flame photometrists is the interference of one or more elements in the sample with the one being determined. If a flame type or solvent cannot be found in which such interference does not exist, it must be allowed for by some method, such as adding the interfering element to the standards in order to compensate for the interference.

While the present study was undertaken primarily for the determination of the alkali oxides, it was thought that magnesium and iron could also be determined by adding known amounts of these elements to the standards of Eubank and Bogue (1) without altering their established method of analysis. It was also felt that such standards since they more accurately represented a cement sample, would give rise to even less interference than might be encountered in the ones containing only sodium, potassium and calcium.

### Experimental

This study was made with a Beckman DU spectrophotometer, with a Model 9200 flame attachment equipped with an oxyhydrogen aspirator-burner and a Model 4300 photomultiplier attachment. The flame photometer was modified in the Research Laboratory for use as a recording instrument by following the instructions of King and Priestley (4). A photograph of the equipment is shown in Figure 1. 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.

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

Sodium was determined by the 589  $\mu$  line, potassium by the 768  $\mu$  line, magnesium by the 383  $\mu$  molecular band, and iron by the 386  $\mu$  line.

Calibration standards were prepared to contain each metal in different amounts, chosen to cover the expected concentration range, as in Table 1.

Standard solutions were prepared by first making up stock solutions of the pure oxides and then taking varying amounts of these stock solutions to make up the standards. The standards contained the various compounds in the range of proportions ordinarily found in portland cement. The stock solutions were stored in polyethylene containers for the preparation of future standards or for additional standards to cover a wider range of concentration of the unknown compound.

TABLE 1  
COMPOSITION OF CALIBRATION STANDARDS

Standard No.	Proportions, parts per million				
	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	Fe <sub>2</sub> O <sub>3</sub>	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 standard solutions were aspirated into the flame and their relative emissions plotted to form a calibration curve. The emission value of each of the four oxides in the cement sample was then taken, and its concentration read directly from this curve.

### Results and Discussion

The results of the chemical analysis and flame analysis of the oxides are given in Table 2 and the concordance of results from duplicate samples for both methods in Table 3. These results show that satisfactory concordance was obtained, both between methods, and between duplicates by the same method.

### Conclusion

A great saving in time is realized by this method over that of standard chemical methods. The 18 analyses reported above, including standard

solution preparation, were done in 24 man-hours as opposed to approximately 100 man-hours required for the chemical method.

Subsequent to the original analyses made in connection with this study, 20 samples in the spring of 1956 and 14 in 1957 were tested for the four oxides and reported to the Testing Laboratory at Ann Arbor. As nearly as we can estimate, this resulted in a total saving of about four working weeks of one analyst's time.

#### REFERENCES

- (1) Wm. R. Eubank and R. H. Bogue, "Studies on the Flame Photometer for the Determination of  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  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.

TABLE 2

## RESULTS OF GRAVIMETRIC VS. FLAME PHOTOMETRIC ANALYSES

Sample No.	Na <sub>2</sub> O, Percent			K <sub>2</sub> O, Percent			MgO, Percent			Fe <sub>2</sub> O <sub>3</sub> , 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 3

CONCORDANCE OF  
GRAVIMETRIC AND FLAME PHOTOMETRIC ANALYSES,  
DUPLICATE SAMPLES

Sample No.	Deviation, Percent							
	Na <sub>2</sub> O		K <sub>2</sub> O		MgO		Fe <sub>2</sub> O <sub>3</sub>	
	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



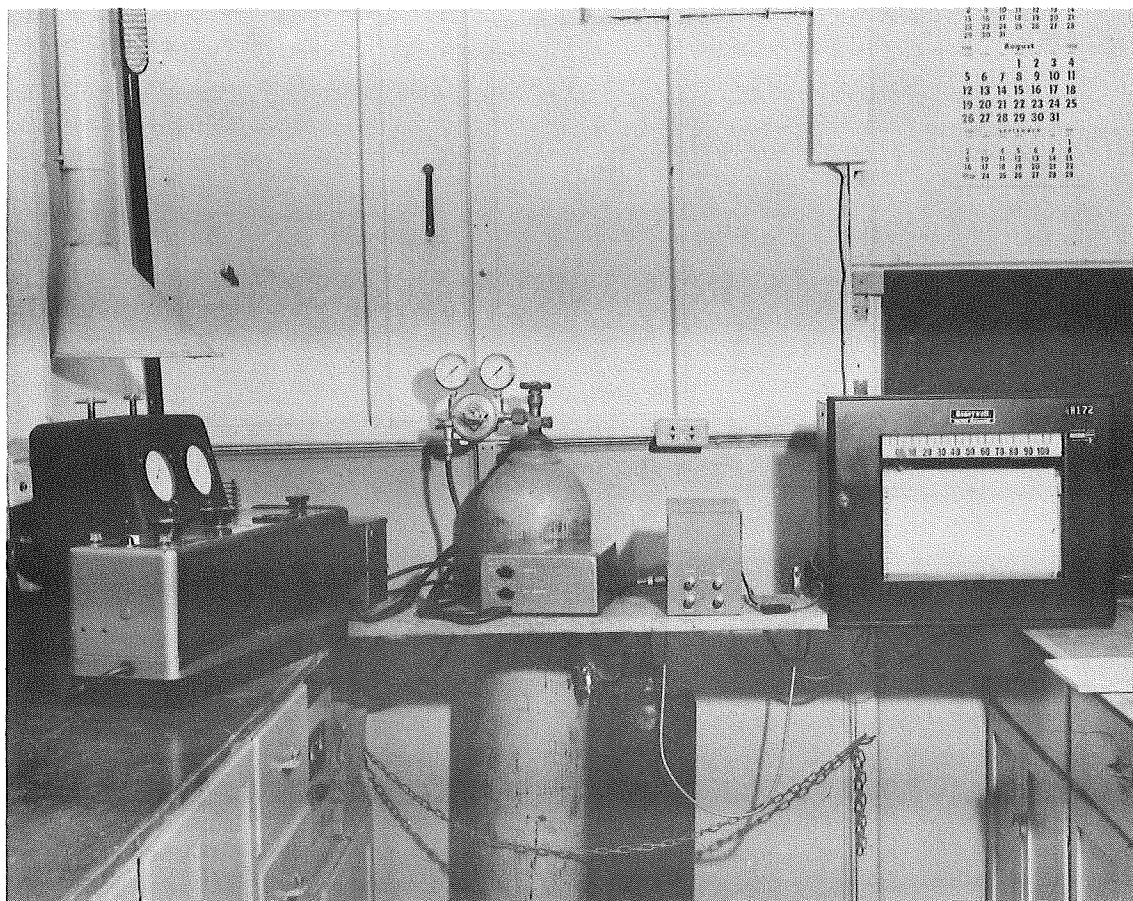


Figure 1. Recording Flame Photometer