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IMPROVEMENTS IN THE RAPID ANALYSIS OF PORTLAND CEMENT BY ATOMIC ABSORPTION SPECTROPHOTOMETRY

B. L. Bean

Federal Highway Administration

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UNITED STATES OF AMERICA

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Final Report

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16. Abstract

A rapid method for analysis of portland cement is given using atomic absorption spectrophotometry (AA), in which either reagent standards or standard cements may be used for calibration purposes. A novel feature of the method is that means are provided for the determination of silica in the same solution as other constituents without further steps or separate solutions. A combination of HF, HCl, and HNO_3, is used to decompose the cement and the excess HF is complexed with H_3BO_3. All solutions must be stored in plastic containers. The concentrated solutions are diluted suitably and AA measurement made with a Perkin-Elmer Model 303 AA spectrophotometer. One weighed portion of the sample is sufficient for the determination of the seven main constituents: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O, and K_2O. Precision data were obtained using reagent standards as well as NBS Standard cements for calibration.

The results obtained in this study are compared with those from two previous cooperative tests of three other proposed atomic absorption methods, and in general, are shown to be better or equivalent. A list of references and 6 Tables are included.

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INTRODUCTION

Many useful applications of atomic absorption spectrophotometry (AA) have been developed since its introduction in 1955 by A. Walsh (1).[1] During 1968 to 1970, the author took part in and helped coordinate two series of cooperative tests on the use of AA for portland cement analysis, conducted in collaboration with the Subcommittee on Materials of the American Association of State Highway Officials (AASHO). That study was under the jurisdiction of Technical Section 3.1 on cement, which had established a Task Force on Rapid Methods of Chemical Analysis. A report describing the results obtained by the cooperating laboratories that took part in these tests has been published (2).

One of the methods described in that report, utilizes standard cements from the National Bureau of Standards (NBS) for preparing calibration curves (3). That method, with only slight modifications, has been adopted by AASHO as an optional method for analysis of cement. In the other two methods studied, standard solutions for calibration were prepared from reagent chemicals. In one of these methods all the silica was put into solution along with the other constituents. In another method, a determination of silica on a separate sample was described. In both of these cases, the silica was present in an acidified solution as silicic acid. Such solutions cannot be stored over any extended period because of the eventual separation of gelatinous silicic acid.

From experience gained in those cooperative tests, it became apparent to the author that it would be desirable to have a more refined method for analysis of cement by AA that would:

(1) be calibrated with standard solutions that can remain stable for months, or even indefinitely;

(2) contain silica in solution and permit its determination along with the other major constituents of cement; and

(3) be based on standard calibration solutions which could be prepared either from chemical reagents or from NBS standard cements, whichever was more convenient to a laboratory.

From an examination of the literature, there appeared to be two possible routes by which these three objectives might be achieved:

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[1] The underlined numbers in parentheses indicate the references listed on pages 27 and 28.

(1) A fusion of cement samples with a suitable chemical flux followed by acidification. (2) Treatment of cement samples with hydrofluoric acid plus either hydrochloric or nitric acid or both, followed by addition of a reagent to complex the excess hydrofluoric acid.

Use of Fluxes for Decomposition

Lithium metaborate ($LiBO_2$), lithium tetraborate ($Li_2B_4O_7$) and a mixture of the two, have been recommended as fluxes for decomposing rocks, minerals, and silicates (4), (5), prior to analysis. Brown, MacKay, and Turek (6), made fusions at 1200°C using lithium tetraborate as a flux and reported that after treatment with hydrochloric acid, the resultant solutions had a shelf life of 3 to 4 months.

Use of Hydrofluoric Acid as Decomposing Agent

Langmyhr and Graff (7) were probably the first to use hydrofluoric acid to decompose silicate rocks followed by a determination of silicon on the resultant solution. They demonstrated that the decomposition process at room temperature results in only a negligible loss of silicon. The excess HF must be either removed or complexed. These authors confirmed work by Tarutani (8) that aluminum salts are more effective for complexing HF than boric acid. In an earlier paper (9) they pointed out that after they had complexed excess HF using a solution of boric acid, their solutions of α - silicomolybdic acid in volumetric flasks exhibited an increase in silica concentration upon standing, due to attack on the glass. This increased concentration did not occur when they changed to the use of $AlCl_3$ as the complexing agent.

Wilson (10) decomposed silicate minerals with hydrofluoric acid prior to determining ferrous iron. He pointed out that there is a tendency for insoluble fluorides to form unless the solutions are kept quite acid. He recommended at least 4 N sulfuric acid. He found that addition of boric acid served the double purpose of bringing insoluble fluorides back into solution and protecting glassware against attack.

Roos and Price (11) reported that 2 g of boric acid to 1 ml of 40 percent hydrofluoric acid was found to prevent precipitation of lanthanum fluoride when 20 ml of 5 percent lanthanum solution was added. When this author attempted to follow this procedure, it was found that a copious white precipitate resulted. In personal correspondence with the senior author, (Roos), it was learned that 5 ml of 30 percent hydrochloric acid was also required in the solution of HF + H_3BO_3 + $LaCl_3$ to prevent precipitation. This author confirmed the latter finding. Roos and Price used plastic beakers for decomposition of the sample, but apparently made dilutions to volume in glass. They used reagent chemicals as standards.

Bernas (12) described a method for decomposition of silicates of tektite type for AA analysis. He developed a decomposition vessel in which the sample was in contact with a Teflon crucible, the latter being supported by a corrosion resistant steel outer container. The sample was treated in the sealed container with a mixture of aqua regia and hydrofluoric acid for 30 to 40 minutes at 110°C. In as much as plastic volumetric flasks were not yet available, Bernas added boric acid, diluted to volume in a glass volumetric flask, and transferred the solution to a polyethylene container. He cautioned that the solutions should not remain in a glass container for longer than two hours. He used reagent chemicals as standards.

Tenoutasse, DeDonder, and Smitz (13), described a method for analyzing cement by AA in which they decomposed the sample at room temperature with a mixture of HCl and HF, then added HNO_3 and H_3BO_3 solution. The solution was then diluted in a glass volumetric flask and transferred **immediately** to a polyvinyl container. They used reagent chemicals as standards. In the work reported in that paper, they used rather concentrated solutions in which calcium was measured (about 160 ppm CaO), and recommended turning the burner 90 degrees to shorten the path of the radiation through the flame.

In a later paper (14), Tenoutasse and DeDonder refined their procedures somewhat. They emphasized the use of "bracketing" and used greater dilutions in which to measure the elements. In bracketing, three solutions are used: a standard solution containing a little less of the constituent than the sample, one containing a little more of the constituent, and the sample solution on which the constituent is being determined. In this study they used only the nitrous oxide burner for all elements regardless of whether air or nitrous oxide was being used as the oxidant and kept the burner in the parallel position for all measurements. They determined ten elements and quoted excellent precision values. It is not clear on what basis these standard deviations were obtained: whether on separate samples weighed out on different days, or on repeated determinations using the same solutions. The number of determinations is also not stated.

Choice of Decomposition Method

When using a fusion technique to decompose the sample, a flux to sample ratio between 10 and 20 is generally recommended. After neutralization with acid, the resultant solution contains a rather high concentration of salts. When the author investigated fusion techniques, there was a tendency for the burner to become clogged. This reduced the precision of measurements being made. Also, the time required to dissolve the fused material seemed excessive.

When a mixture of hydrofluoric, hydrochloric, and nitric acids is used to decompose the sample, followed by the addition of boric acid as a complexing agent, the ratio of boric acid to sample weight is generally about 7. $AlCl_3$ could not be used as the complexing agent because it was necessary to determine aluminum.

For these reasons, most of the work included in the study reported here utilized a mixture of hydrochloric, hydrofluoric, and nitric acids to decompose the sample. Boric acid was added to complex excess hydrofluoric acid and help protect glassware where glass was used.

For the purpose of this study, it was decided to concentrate on the determinations of seven of the constituents of cement by AA: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, Na_2O and K_2O. In the first part of the study, reagent chemicals were used to prepare standard solutions for calibration purposes. From calculations, it was decided to base the concentrations of the stock reagent standard solutions (concentrated solutions containing mixtures of the primary reagent standards) on a 0.3000 g sample of cement in 100 ml of solution. This would make it possible, by appropriate aliquoting procedures, to obtain diluted solutions for AA measurements which would keep the response of absorbance to concentration in a linear range for all the constituents to be measured. These conditions put limitations on the concentrations of primary reagent standards to be used. NBS standard cements, Nos. 1011, 1013, 1015, and 1016 were selected to be used as unknowns, and it was planned to determine by AA the seven constituents listed.

In the second part of the study, NBS standard cements, Nos. 1011, 1013, 1014, and 1015 were used as standards and were dissolved (the concentrated solutions referred to as stock cement standard solutions) in in exactly the same manner as the cement samples to be analyzed. In this phase, determinations were made on NBS standard cements, Nos. 177 and 1016.

SPECIAL INSTRUMENTATION CONSIDERATIONS

The apparatus used is listed in Appendix A. The Perkin-Elmer (P-E) Model 303 Atomic Absorption Spectrophotometer (Model 303), (15), which was used for the work reported in this study, had been modified by replacing the original burner and mount with an improved burner and mount, Part No. 303-0410, and the original stainless steel nebulizer with an improved corrosion resistant nebulizer, 303-0404. An attachment called a Model DCR1 Digital Concentration Readout, Part No. 303-0177, (DCR1)(16), which provided a four-digit readout on an illuminated counter, was used in conjunction with the Model 303.

The DCR1 conveniently enables the absorbance to be read directly, without first taking an absorption reading and then finding the absorbance equivalent by reference to a table. The relationship between absorbance and absorption is:

$$\text{Absorbance} = \log_{10}\left(\frac{100}{100 - \%\ \text{absorption}}\right).$$

Concentration is

generally proportional to absorbance, not to absorption. It is also possible to obtain readings that are multiples (or submultiples) of the absorbance, by using the CONCENTRATION mode.

One observation on the use of the DCR1 should be made at this point. In the author's experience with this readout device there is no advantage to using a zero suppression technique as far as accuracy and variability are concerned. For example, when determining CaO in cement, it might seem advantageous, if such "zero suppression" adjustments are available, to set the instrument to read near zero when a solution derived from a low-lime cement that contains 60% CaO is being nebulized, and to read a high number when a solution from a high-lime cement that contains 67% CaO is being nebulized. In other words, this would expand the readings over the range of expected composition. This technique has been recommended by some investigators and it would seem to be desirable for sensitivity in the case of a major constituent. There probably are readout devices which provide useful zero suppression. In this study, however, when zero was suppressed (Using the ABS ZERO SET knob), the variability was not affected. In Table 1, it can be seen that expanding scale expands the standard deviation, also that after zero has been suppressed, the standard deviation remains essentially the same as before. There may be some advantage to using scale expansion, although probably not much. For a cement containing 67.0% CaO it would seem advisable to be able to obtain absorbance or concentration readings significant to 1 part in 670. It may be easier to do this if the readout is 1.624 rather than 0.309.

Some difficulties were experienced when using the nitrous oxide burner head provided by the manufacturer for the Model 303. When using a nitrous oxide-acetylene flame to determine refractory elements such as silicon and aluminum, carbon deposits formed on the burner slot and interfered with the flame. These deposits could be scraped off with a carbon rod but tended to reform and interfere again during the aspiration of a sample. A Techtron nitrous oxide burner head (Model AB-50)[2] which had been recommended by Rains (17), was found to be effective in minimizing the formation of these carbon deposits. This burner head is constructed with grooves on both sides of the slit. The grooves are about 10 mm wide, 5 mm deep, and have sloping sides. The slit is about 8 mm longer than that of the burner head formerly used, a feature which increases sensitivity somewhat. A stainless steel adapter was constructed to enable the Techtron burner head to be used with the P-E burner and mount, Part No. 303-0410.

Two other burner heads manufactured by P-E were used. One was a 3-slot Boling burner head for air-acetylene mixtures. The other was a

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[2] Obtained from Aerograph Division of Varian Associates, 1500 King's Highway, Cherry Hill, New Jersey 08034

Table 1. Illustrations of Use of Scale Expansion and Zero Suppression with DCR1 [a]

Reading Number	Reading Mode		
	Absorbance (no scale expansion)	Concentration (scale expanded 5.25 times, no zero suppression used)	Concentration (same scale expansion, with zero suppression)
1	.309	1.626	0.320
2	.308	1.622	.307
3	.308	1.624	.303
4	.309	1.629	.299
5	.310	1.628	.302
6	.311	1.636	.306
7	.310	1.625	.309
8	.307	1.611	.302
9	.308	1.613	.296
10	.310	1.625	.291
Average	$0.309 = 3.09 \times 10^{-1}$	1.624	$0.304 = 3.04 \times 10^{-1}$
s^2	1.550×10^{-6}	5.388×10^{-5}	6.206×10^{-5}
s	1.25×10^{-3}	7.3×10^{-3}	7.9×10^{-3}

[a] Readings obtained from 12.86 ppm CaO solution.
P-E N_2O burner used; Flow: air-5, C_2H_2-5.7.
Wavelength = 4227 A, Slit 4, Noise suppression 2.
Each reading was obtained with the AVERAGE knob in the 16 x position.

burner head designed for use with nitrous oxide. It had a single, 52 mm slot and was used with air-acetylene for the determination of calcium. In this determination use of the single slot burner provided less sensitivity but better precision than the Boling burner. The flame produced by the nitrous oxide burner head was steadier.

Early investigators have inferred that H_3BO_3 complexes excess HF and thus protects glass containers and permits their use without causing errors because of the decomposition of glass by HF. Attempts in this study to use glass volumetric flasks with solutions containing HF plus H_3BO_3 gave very disappointing results. This corroborates the findings of Langmyhr and Graff as well as Tarutani and others that boric acid does not completely complex HF and therefore does not entirely protect glass from **being attacked** by such solutions. Polypropylene volumetric flasks as well as 10- and 25-ml burets made of the same material, became available during the course of this study. Thereafter, polypropylene volumetric equipment was used wherever feasible.

RESULTS

Details of the method developed and used in this study **are given** in Appendix A. Table 2 includes the results obtained for the NBS Standard Samples of cement, Nos. 1011, 1013, 1015, and 1016, using the procedure and stock reagent standard solutions. Each determination represents a separate weighed portion of the cement sample. Six determinations were made of each constituent on the four samples. Also given in Table 2 are the averages, the NBS certificate values, the differences (AA percent-certificate percent), the standard deviations, and the pooled standard deviations. Two sets of stock reagent standard solutions were used, each containing 100 ml.

Table 3 includes the results obtained when analyzing NBS Standard Samples 1016 and 177, using as standards NBS Standard Samples 1011, 1013, 1014, and 1015. In this case the cements selected as standards were put into solution in the same manner as the two cements selected as unknowns. Two sets (100 ml each) of stock cement standard solutions were used. The cements used as standards did not contain enough Na_2O. Therefore 1.200 and 0.480 ml of 1,000 ppm Na_2O solution were added to the solutions containing the samples of NBS 1013 and 1014 respectively, causing these solutions, to contain the equivalents of 0.60 and 0.40 percent Na_2O. Individual samples of cements NBS Nos. 1016 and 177 were weighed out on different days so **each** determination given in Table 3 represents a separate **sample.** Six determinations of each constituent were made for each cement. Also given in Table 3 are the averages, the NBS certificate values, the differences (AA percent - certificate percent), the standard deviations and the pooled standard deviations for the two samples, for each constituent.

Table 2. AA Analysis of NBS Standard Cements Using Reagent Standards

Detn. No.		SiO_2, percent	Al_2O_3, percent	Fe_2O_3, percent	CaO, percent	MgO, percent	Na_2O, percent	K_2O, percent
				NBS 1011				
1.		20.84	5.24	2.00	66.77	1.12	0.08	0.26
2.		20.90	5.30	2.02	66.53	1.03	0.07	0.27
3.		20.90	5.32	2.01	67.40	1.05	0.07	0.27
4.		21.17	5.35	2.00	66.40	1.06	0.07	0.26
5.		20.90	5.32	2.00	66.58	1.04	0.07	0.27
6.		20.75	5.33	2.00	66.46	1.03	0.08	0.27
	s	0.14	0.04	.008	0.37	0.03	0.005	0.005
	average AA	20.91	5.31	2.00	66.69	1.06	0.07	0.27
a/	certificate	21.13	5.38	2.07	66.49	1.12	0.08	0.26
b/	difference	-0.12	-0.07	-0.07	+0.20	-0.06	-0.01	+0.01
				NBS 1013				
1.		24.28	3.27	3.00	64.34	1.46	0.20	0.33
2.		24.36	3.22	3.00	64.22	1.32	0.20	0.32
3.		23.87	3.22	2.96	64.30	1.33	0.19	0.31
4.		23.95	3.23	2.95	64.30	1.36	0.19	0.32
5.		24.14	3.29	2.97	64.00	1.32	0.19	0.33
6.		24.10	3.24	2.98	63.71	1.33	0.22	0.32
	s	0.19	0.03	0.02	0.25	0.05	0.01	0.008
	average AA	24.12	3.24	2.98	64.15	1.35	0.20	0.32
a/	certificate	24.17	3.30	3.07	64.26	1.39	0.20	0.32
b/	difference	-0.05	-0.06	-0.09	-0.11	-0.04	0.00	0.00

continued - next page

Table 2. AA Analysis of NBS Standard Cements Using Reagent Standards (continued)

Detn. No.		SiO_2, percent	Al_2O_3, percent	Fe_2O_3, percent	CaO, percent	MgO, percent	Na_2O, percent	K_2O percent
				NBS 1015				
1		20.41	4.90	3.21	60.70	4.22	0.17	0.86
2		20.70	4.89	3.23	61.18	4.20	0.15	0.87
3		19.95	4.87	3.20	60.80	4.27	0.16	0.87
4		20.66	4.89	3.20	61.80	4.20	0.15	0.88
5		20.70	4.87	3.17	61.05	4.17	0.15	0.87
6		20.22	4.95	3.17	61.27	4.23	0.17	0.88
	s	0.31	0.03	0.02	0.39	0.03	0.01	0.008
	average AA	20.44	4.90	3.20	61.13	4.22	0.16	0.87
a/	certificate	20.65	5.04	3.27	61.37	4.25	0.16	0.87
b/	difference	-0.21	-0.14	-0.07	-0.24	-0.03	0.00	0.00
				NBS 1016				
1		20.75	4.56	3.64	64.61	0.35	0.59	0.05
2		21.05	4.55	3.66	64.84	0.35	0.57	0.04
3		20.90	4.56	3.61	64.87	0.35	0.56	0.03
4		20.96	4.51	3.63	64.52	0.34	0.57	0.04
5		20.90	4.53	3.60	(66.56) c/	0.37	0.56	0.04
6		20.47	4.60	3.58	64.40	0.35	0.59	0.04
	s	0.20	0.03	0.03	0.20	0.008	0.01	0.006
	average AA	20.84	4.55	3.62	64.65	0.35	0.57	0.04
a/	certificate	21.05	4.97	3.71	65.01	0.42	0.55	0.04
b/	difference	-0.21	-0.42	-0.09	-0.36	-0.07	+0.02	0.00
	pooled s	0.22	0.03	0.02	0.32	0.04	0.01	0.01

a/ Certificate = NBS certificate value for constituent, percent

b/ Difference = **(AA percent - certificate percent)**

c/ This value obtained in the 5th determination for CaO was eliminated from calculations using the criteria recommended by Dixon and Massey (18). Therefore the calculations for CaO in NBS 1016 were based on 5 determinations.

Table 3. AA Analysis of NBS Standard Cements Using Other NBS Cements as Standards

Detn. No.		SiO_2, percent	Al_2O_3, percent	Fe_2O_3, percent	CaO, percent	MgO, percent	Na_2O, percent	K_2O, percent
				NBS 1016				
1.		20.95	4.69	3.70	65.39	0.43	0.55	0.05
2.		20.87	4.69	3.69	65.43	0.42	0.53	0.04
3.		20.90	4.64	3.67	65.00	0.43	0.54	0.03
4.		20.89	4.69	3.73	65.26	0.42	0.55	0.03
5.		21.10	4.66	3.71	65.62	0.46	0.54	0.03
6.		21.01	4.68	3.61	64.38	0.40	0.53	0.05
	s	0.09	0.02	0.04	0.44	0.02	0.009	0.01
	average	20.95	4.68	3.68	65.18	0.43	0.54	0.04
	certificate	21.05	4.97	3.71	65.01	0.42	0.55	0.04
	difference	-0.10	-0.29	-0.03	+0.17	+0.01	-0.01	0.00
				NBS 177				
1.		21.93	5.26	2.40	63.70	2.45	0.13	0.55
2.		21.92	5.25	2.42	64.00	2.47	0.15	0.56
3.		22.15	5.21	2.42	64.00	2.47	0.14	0.56
4.		21.80	5.33	2.45	64.27	2.43	0.12	0.56
5.		21.96	5.28	2.44	64.70	2.47	0.13	0.55
6.		21.87	5.22	2.38	63.03	2.41	0.12	0.54
	s	0.12	0.04	0.03	0.56	0.03	0.01	0.008
	average	21.94	5.26	2.42	63.95	2.45	0.13	0.55
	certificate	21.92	5.27	2.39	64.27	2.45	0.14	0.57
	difference	+0.02	-0.01	+0.03	-0.32	0.00	-0.01	-0.02
	pooled s	0.10	0.03	0.03	0.51	0.02	0.01	0.01

Discussion of Results

An examination of the results given in Table 2 shows that the average difference between AA results and the certificate value (AA percent - certificate percent) was -0.15 percent for SiO_2, -0.17 percent for Al_2O_3, and -0.13 percent for CaO. The average difference for all constituents was -0.08 percent.

Consideration of the results given in Table 3 shows that the average difference between AA results and the certificate value (AA percent - certificate percent) was -0.04 percent for SiO_2, -0.15 percent for Al_2O_3, and -0.08 percent for CaO. The average difference for all constituents was -0.04 percent.

There was a tendency for a small negative bias between AA results and the certificate value with this bias being less when using cement standards than when using reagent standards. The reasons for this are not clearly understood.

It is of interest to compare the precision of the results given in Tables 2 and 3 with that of the best results obtained in a previous study, Ref. (2)(Round 2). This will be referred to in this paragraph as Method I. In the latter, pooled within laboratory **standard deviations** are given for two cements. The following conclusion is based on comparisons of the variances from which the standard deviations in Method I were obtained with the variances on which the pooled standard deviations in the present Tables 2 and 3 were obtained, using the F statistic (19). Use of the method described in this study gave precision better than or equivalent to Method I for all constituents determined except CaO. Method I is the method which has been adopted as an optional method by the Subcommittee on Materials of AASHO.

The AA results reported for Al_2O_3 in NBS 1016 indicated an appreciable negative bias from the certificate value of 4.97 percent. The reason for this is not clear. Addition of La so that standard and sample solutions contained 1 percent La, helped very little. Addition of 2,000 ppm Cs or 1,000 ppm K did not improve the situation. Evidently the presence of about 350 ppm of Ca eliminates ionization effects so that addition of Cs or K serves no useful function.

It was noted that NBS 1016 has the lowest MgO and highest TiO_2 content of any of the NBS Standard cements. Standard Mg solution and standard Ti solution were added to separate samples of NBS 1016. No appreciable effect on Al results was noted. Unfortunately, neither Roos and Price (11), nor Tenoutasse and DeDonder (14), published results for NBS 1016, only results for 1013, 1014 and 1015.

A deuterium arc compensation system has been described (20) and is commercially available. It is said to correct for background absorption where the method of standard addition, which was also tried in this study, does not compensate completely for this type of interference. It is possible that use of such an attachment would be beneficial for the determination of Al_2O_3 in cement. The instrument used for this study was not so equipped.[3] This possibility may be explored later.

CONCLUSIONS

In this study, a method was developed for the determination of the seven constituents of portland cement by AA analysis. Both reagent chemicals and NBS Standard cements were used to prepare calibration curves with satisfactory results. The stock (concentrated) standard and sample solutions remained stable at least six months and may remain so indefinitely. Use of a mixture of HCl, HF, HNO_3, and H_3BO_3 decomposed the cement and kept the silica in solution. The H_3BO_3 complexed most of the excess HF. All solutions containing HF were, however, stored in containers made of some type of plastic. For measurement of such solutions, rigid polypropylene volumetric flasks and burets were used. Special precautions were required when using these flasks and burets.

The time required for nebulization of a test solution to obtain a proper reading was about 15 seconds. The values reported in Tables 5 and 6 were averages of three such readings. Preparation of stock standard and sample solutions, aliquoting, as well as the dishwashing associated with the entire procedure require careful organization of the work. The dishwashing and preparation of most of the solutions could be done by a technician. In this study, the main emphasis was on the accuracy and precision of results. Use of this AA method can do much to speed up the analysis of portland cement. When large numbers of samples of cement need to be analyzed use of this method should reduce the costs of testing. There are automatic aliquoting machines on the market which should prove useful in such situations. With such aliquoting machines and proper organization of the work it should be possible to analyze portland cement for all the seven constituents in approximately three hours.

The procedure which was described in this report, gave results for all constituents, except CaO, which were either better than or equal to the results obtained in two studies previously reported (2). According to the AA procedure which gave the best results in that report and has been accepted by the Subcommittee on Materials of AASHO, SiO_2 must be determined on a separate sample. In the procedure developed in this study, SiO_2 can be determined from the same stock solutions which contain the other constituents. This fact should reduce further the time required for AA analysis of cement.

APPENDIX A
Method of Analysis of Cement by Atomic Absorption Spectrophotometry

Scope

This method describes the determination of silicon dioxide, aluminum oxide, ferric oxide, calcium oxide, magnesium oxide, sodium oxide, and potassium oxide in portland cement by atomic absorption spectrophotometry. For calibration purposes either solutions prepared from reagent chemicals or solutions prepared from NBS standard cements are utilized.

Apparatus

A Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer equipped with a P-E Model DCR1 Digital Concentration Readout. A three-slot air-acetylene burner head, a 52 mm short path air-acetylene burner head, and a Techtron nitrous oxide burner head. If other equivalent instruments are used, these directions may need to be modified in accordance with the directions provided by the manufacturer of the instrument being used. Other equipment includes a 500 VA constant voltage transformer, a vent for removing the fumes from the burner, a supply of clean, dry, oil-free compressed air at 60 psi, and cylinders of acetylene and nitrous oxide.

Nomenclature for Solutions Used

1. When a definite weight of a solid reagent chemical has been put into a fixed volume of solution, the latter is referred to as a primary reagent standard. For example, a 2,000 ppm MgO solution.

2. When a definite volume, for example 100-ml, of a concentrated solution, representing a definite weight of cement is prepared, this will be referred to as a stock solution. The solutions to be measured by AA are dilutions of stock solutions. The stock solution may be prepared from primary reagent standards, in which case it will be referred to as a stock reagent standard solution. It may be prepared from an NBS standard cement, in which case it will be referred to as a stock cement standard solution. Or, it may be prepared from a sample of cement to be analyzed, in which case it will be referred to as a stock sample solution.

3. After stock solutions have been diluted according to the flow chart shown in Figure 1, they will be referred to as calibration reagent solutions, calibration cement solutions, or test sample solutions.

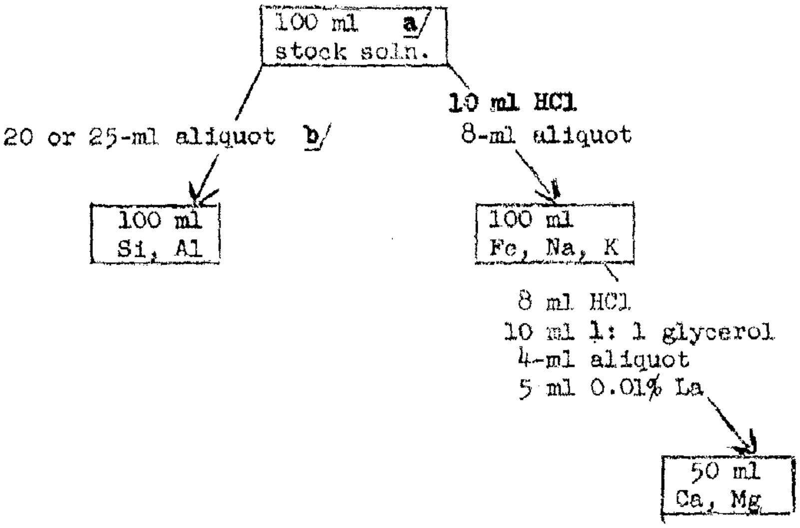

Figure 1. Analytical flow chart for preparing calibration and test sample solutions from stock solutions.

a/ Multiples of 100 ml of stock solutions may, of course, be prepared for stock reagent or stock cement standards. 100 ml is adequate for stock sample solutions.

b/ By using two 25-ml aliquots and one 20-ml aliquot at this point, three sets of calibration reagent or calibration cement solutions can be prepared from 100 ml of stock solution, if dry pipets are used.

4. Solutions of boric acid, lanthanum, and glycerol are referred to as special solutions.

Primary Reagent Standards

SiO_2 solution, approximately 2,000 ppm: Dry silicon dioxide, (99.9999%) (may be obtained from SPEX Industries, Inc., Metuchen, N. J.) at 150-170°C. Weigh by difference and transfer about 2.1 g of this SiO_2 into a 1-liter wide mouth, screw cap, polypropylene bottle. Add 40.8 ml of 49% HF using a polypropylene graduated cylinder. Screw the cap tightly on the bottle. Swirl the contents of the bottle several times, place it gently on its side and roll it so that almost all the inside surface of the bottle is wet. Do not shake the bottle. Allow it to stand upright overnight. Then unscrew the cap and add 525 ml of filtered 5% boric acid solution. Let it stand 1 hour with occasional swirling. Transfer to a 1-liter polypropylene volumetric flask by pouring through a polypropylene funnel. Wash the bottle and funnel thoroughly, adding the washings to the flask. After cooling to room temperature, dilute the solution to the mark and mix thoroughly. As an example, if a portion of SiO_2 weighing 2.0629 g is treated as described, it will give a solution containing 2,062.9 ppm SiO_2. Store the solution in a 1-liter polyethylene bottle.

Al_2O_3 solution, 4,000 ppm: Weigh exactly 2.1191 g of aluminum wire, (if 99.9% Al), transfer to a 600-ml beaker, treat with 200 ml of water, 21.2 ml of HCl(sp gr 1.19) and 4 drops of saturated H_gCl_2. Cover the beaker with a watch glass, heat about an hour and allow to stand overnight. Heat on a hot plate again until all action is completed. Cool, filter into a 1-liter volumetric flask and wash the beaker and filter thoroughly. A small drop of Hg will remain on the filter. Use of $HgCl_2$ speeds up solution of the Al in HCl. After the solution has cooled, dilute to the mark, mix thoroughly, and store in a 1-liter polyethylene bottle.

Fe_2O_3 solution, 4,000 ppm: Weigh exactly 2.8032 g of iron wire (if 99.8% Fe). Treat in a beaker with water and 22.2 ml of HNO_3 (sp gr 1.42). Cover the beaker with a watch glass and heat until all the iron has dissolved. Cool, filter into a 1-liter volumetric flask and wash the beaker and filter thoroughly. Dilute to the mark and transfer to a 1-liter polyethylene bottle.

CaO solution, 16,000 ppm: Weigh exactly 57.5734g of low alkali calcium carbonate, (if 99.2% $CaCO_3$), and transfer to a 3-liter beaker. Treat with about 600 ml of water and 98 ml of HCl. Stir the contents of the beaker carefully until all reaction appears to cease. Cool the solution, and filter into a 2-liter volumetric flask. Wash the beaker and filter thoroughly. Dilute the solution to the mark, mix and transfer to a 2-liter polyethylene bottle.

MgO solution 2,000 ppm: Weigh exactly 1.2086 g of magnesium powder (99.8%)(may be obtained from Alfa Inorganics, Beverly, Mass.) and transfer to a 600-ml beaker. Treat with 150 ml of water and then 9.9 ml of HCl. When action has subsided, cool the solution and filter into a 1-liter volumetric flask. Wash the beaker and filter thoroughly. Dilute the solution to the mark and transfer to a 1-liter polyethylene bottle.

Na_2O solution 1,000 ppm: Weigh exactly 1.8897 g of sodium chloride (assuming 100%) which has been dried overnight at 105°C, dissolve in water, quantitatively transfer to a 1-liter volumetric flask, and dilute to the mark. Transfer the solution to a 1-liter polyethylene bottle. To prepare an Na_2O solution, 100 ppm, dilute this 1,000 ppm Na_2O solution 1:10 (for example, dilute 100 ml of 1000 ppm Na_2O solution to 1 liter).

K_2O solution 1,000 ppm: Weigh exactly 1.5861 g of potassium chloride (assuming 100%) which has been dried overnight at 105°C, dissolve in water, quantitatively transfer to a 1-liter volumetric flask, and dilute to the mark. Transfer the solution to a 1-liter polyethylene bottle. To prepare a K_2O solution, 100 ppm, dilute this 1,000 ppm solution 1:10 (for example, dilute 100 ml of 1,000 ppm K_2O solution to 1 liter).

Special Solutions

Boric Acid, 5% solution: Treat 100 g of boric acid crystal, in a 2-liter beaker with about 1,600 ml of water. Heat the mixture and stir until all is in solution. Allow to cool somewhat and transfer quantitatively into a 2-liter volumetric flask using a funnel. Dilute almost to the mark, cool to room temperature, dilute to the mark, mix and transfer to a 2-liter polyethylene bottle.

Lanthanum, 0.01% La solution: Weigh exactly 0.1173g of La_2O_3 (assuming 99.99%), place in a 150-ml beaker and treat with 2 ml of 1:1 HCl. Cover the beaker with a watch glass and heat cautiously until almost everything appears to be in solution. Wash the beaker and watch glass with water until the volume is about 25 ml. Heat the solution further for about a minute, then allow to cool. Filter into a 1-liter volumetric flask and wash the beaker and filter thoroughly. Cool the solution, dilute to the mark, mix and transfer to a 1-liter polyethylene bottle. Use of this dilute solution of lanthanum in conjunction with glycerol is recommended by Rains (21) for releasing the alkaline earth metals in the presence of aluminum (removing the aluminum interference). When the higher concentrations of lanthanum alone, usually recommended for this purpose, are used, burner clogging is likely to occur.

Glycerol solution, 1:1. Mix reagent grade glycerol with an equal volume of water.

Preparation of Stock Reagent Standard Solutions

The relative compositions of 4 synthetic portland cements are given in Table 4. The compositions of these cements are to be produced by using appropriate amounts of the primary reagent standards whose preparation has been described above.

The number of ml of each reagent standard to be used to produce 100 ml of each of the 4 standards are given in Table 5. Obviously, multiples of 100 ml of the standards may be prepared, if desired. It will be noted that HCl, HNO_3, and H_3BO_3 are added to each standard stock solution in appropriate amounts so that the concentrations with respect to these acids will be the same as in the sample solutions.

If it is desired to include the determination of SrO, Mn_2O_3 and TiO_2 in the analyses, suitable volumes of reagent standards of these constituents should be added to the volumes of reagent standards given in Table 5, taking care that a total volume of 100 ml not be exceeded. If such an eventuality does appear likely, some of the reagent concentrations would have to be increased above those in Table 5, so that the total volume can be kept below 100 ml. Prepare all the stock reagent standard solutions in polyethylene volumetric flasks and either store them that way or transfer to bottles made of the same material. Use a plastic buret to measure the SiO_2 solutions. Glass burets or pipets may be used to measure the other primary reagent standard solutions.

Preparation of Stock Cement Standard Solutions

Select at least four NBS standard cements that will cover the range of the elements to be determined in the samples to be analyzed. Weigh a 0.3000 g sample of each standard portland cement to within 0.1 ml, and transfer to a 250-ml Teflon beaker. Treat with 10 ml of water and 13.25 ml of HCl and stir with a Teflon coated stirring rod until the cement is decomposed. Then, in a hood, add 1.50 ml of 49% HF by means of a 10-ml plastic buret. Stir the solution and then let stand with occasional stirring for about 15 minutes. Add 40 ml of 5% H_3BO_3 and 1.0 ml of HNO_3. Stir the sample occasionally for another 15 minutes, and then transfer through a plastic funnel to a 100-ml plastic volumetric flask. Cool the contents of the flask and dilute to the mark. The contents of this flask are here referred to as a stock cement standard solution.

Table 4. Percentage of Constituent in four Stock Reagent Standard Solutions (Synthetic Cements) [a/]

Stock Reag. Std. Soln. No.	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O
1	60	24	2	1	5	0.05	1.00
2	62.5	18	4	2	3	.25	0.75
3	65	20	6	4	1	.75	.25
4	67.5	22	8	6	0.5	1.00	.05

[a/] The percentage values given in this table are the values used to plot the percentages of a constituent when **preparing** calibration curves (assuming that the stock reagent standard solutions are prepared according to the directions given in Table ~~3~~). 5

Table 5. Instructions for Preparing Stock Reagent Standard Solutions

(Volume of primary reagent standard required to prepare 100 ml a/ of stock reagent standard solution as though from 0.3000 g of cement in Table 2)
4

Stock Reag. Std. Soln. No.	CaO, ml of 16,000 ppm	SiO_2, ml of 2,062.9 ppm	Al_2O_3, ml of 4,000 ppm	Fe_2O_3, ml of 4,000 ppm	MgC, ml of 2,000 ppm	Na_2O, ml aliq./reag. std.	K_2O, ml aliq./reag. std.	Finally add the following:
1.	11.25	34.90	1.50	0.75	7.50	1.50/100 ppm	3.00/1,000 ppm	b,c/
2.	11.72	26.18	3.00	1.50	4.50	0.75/1,000 ppm	2.25/1,000 ppm	b,d/
3.	12.19	29.09	4.50	3.00	1.50	2.25/1,000 ppm	0.75/1,000 ppm	b,e/
4.	12.66	31.99	6.00	4.50	0.75	3.00/1,000 ppm	1.50/100 ppm	b,f/

a/ Multiples of 100 ml of these stock solutions may, of course, be prepared.
b/ Then to each 100 ml volumetric flask, add 12.50 ml HCl and 1.0 ml HNO_3.
Then (based on use of 2,062.9 ppm SiO_2 soln.) add:*
c/ 21.68 ml of 5% H_3BO_3 to No. 1
d/ 26.26 ml of 5% H_3BO_3 to No. 2
e/ 24.73 ml of 5% H_3BO_3 to No. 3
f/ 23.20 ml of 5% H_3BO_3 to No. 4

Dilute to the mark and mix thoroughly.

*The number of ml of 5% H_3BO_3 to add to each solution

$$= \frac{2 - (\text{ml } SiO_2 \text{ solution used} \times 0.02625)}{0.05}$$

where 2 = g H_3BO_3 added to each sample stock solution,
0.02625 = 525 x 0.05 x 10^{-3} = g of H_3BO_3 used per ml of ca. 2,000 ppm SiO_2 solution,
and 0.05 = g of H_3BO_3 per ml of 5% H_3BO_3.

If the values for a given element (expressed as the oxide) in the NBS standard cements, do not extend over a sufficient range for the purpose of the samples to be analyzed, before dilution add sufficient primary reagent standard solution of the element in question to one or two of the stock cement standard solutions to bring the total content of the element to the desired value(s). For example, addition of 1.200 and 0.480 ml of 1,000 ppm Na_2O solution to the solutions containing the stock cement standards for NBS 1013 and 1014 respectively, in 100 ml of solution, will cause these solutions to contain the equivalents of 0.60 and 0.40 percent Na_2O.

Preparation of Stock Sample Solutions

Prepare stock sample solutions in exactly the same manner as described in the preceding paragraph for the preparation of Stock Cement Standard Solutions.

Dilution of Stock Solutions

After the stock reagent or cement standard solutions and stock sample solutions have been prepared, dilutions of each for AA measurement should be made according to the analytical flow chart shown in Figure 1. This provides concentrations of the elements within the working ranges recommended as being linear by the manufacturer of the instrument. The absorption measurements should be made as soon as possible after the aliquoting procedure. After using a glass pipet with any solution containing HF plus H_3BO_3, the pipet should be rinsed immediately with tap water to minimize the time of contact between the glass and the solution. Allowing the diluted solutions to stand overnight, does not appear to cause any detectable error. In the aliquots used for calcium and magnesium, some changes in concentration may occur in two to three days. All the other diluted solutions should be stable for several days. The stock solutions appear to remain stable indefinitely, if kept tightly stoppered.

The solutions which have been diluted according to Figure 1, may be identified as calibration reagent solutions, calibration cement solutions, or test sample solutions, depending on the concentrated stock solution from which they were derived.

Instrumental Parameters

The instrumental parameters to be used in making the AA measurements are given in Table 6.

For the constituents other than calcium, the optimum burner height is generally about 3 mm below the point at which the burner

Table 6. Instrumental Parameters

The lamp current used in each instance should be that recommended by the manufacturer of the hollow cathode lamp.
On the DCR1, the AVERAGE is set on 8X, the NOISE SUPPRESSION on 2, and the CURVATURE switch on OFF, except when making preliminary adjustments.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
Wavelength, a/	2516	3093	2483	4227	2852	5890 5896	7665
Burner	Techtron 60 mm slot	Techtron	Boling, 3 slot	P-E, N_2O or 52 mm slot	Boling 3 slot	Boling 3 slot	Boling 3 slot
Flow rates b/	N_2O-6 C_2H_2-5.6	N_2O-6 C_2H_2-5.3	air-10.5 C_2H_2-10.5	air - 5 C_2H_2-5.7	air-10.5 C_2H_2-10.5	air-10.5 C_2H_2-10.5	air-10.5 C_2H_2-10.5
Red Feather c/	38 mm	16 mm	-	-	-	-	-
Slit Setting	3	3	3	4	4	4	4
Filter	Out	Out	Out	Out	Out	Out	In

a/ The wavelengths given are the theoretical values.
The instrument may require slightly different settings to obtain maximum absorption.

b/ In both cases when N_2O is the oxidant, the flow rate for C_2H_2 is indicated by the steel ball.
In all cases when air is the oxidant, the flow rate for C_2H_2 is indicated by the plastic ball.

c/ The zone used for measurement of refractory elements is generally called the "red feather" from the color of that part of the flame.

blocks out the radiation. For calcium, the height for maxium absorption is generally about 10 mm below this point. The burner height setting is much more critical for calcium than for the other elements.

AA Measurements

The procedures recommended by the manufacturer of the instrument should be followed in regard to use of the instrument. All solutions to be nebulized should first be poured into 50-ml polyethylene beakers. In setting the zero reading of the instrument, distilled water should be nebulized and the absorbance set to read a small positive number, generally 0.002 absorbance.

Two preliminary test solutions of the element to be measured should be used. One solution should contain a concentration of the element about midway in the recommended linear concentration range. This solution is used when adjusting the burner position as well as the acetylene and oxidant flow rates. The other test solution should contain a lower concentration of the element, and is used to determine the sensitivity. From the absorbance reading obtained for this dilute solution and the parts per million of the element present (not as the oxide), the sensitivity can be calculated by the formula:

$$\text{Sensitivity (for 1 percent absorption)} = \frac{0.0044 \times \text{ppm of element}}{\text{absorbance}}$$

where 0.0044 = absorbance equivalent to 1 percent absorption. A determination of the sensitivity before each run, gives an indication of the condition of the hollow cathode lamp as well as the general condition of operation of the instrument.

Prior to taking the first reading on the first standard or sample solution, distilled water should be nebulized and the DCR1 readjusted if necessary, to read about 0.002 absorbance. Then repeated readings on the first standard (or sample) are taken until consistent results are obtained. For all the elements, except calcium, absorbance readings are taken of the four standards, and then the samples, in succession. This procedure is carried out three times. The averages of the three absorbance readings obtained for each are then calculated. The value for distilled water is not substracted. For the standards, points are plotted on graph paper with absorbance on the ordinate versus percentage (expressed as the oxide percent) on the abscissa. The value for percentage is that given in Table 4 for each constituent in a reagent standard solution. A curve (generally almost a straight line) is drawn through the points. The percentage of the element in each sample is then read from the respective calibration curve. If cement standard solutions are being used, the value for percentage of each constituent is, of course, the NBS certificate value.

For calcium, a bracketing technique is used. First, single absorbance readings of standards and samples are taken. This gives an indication of the relative concentrations of calcium present. Then the SET CONCENTRATION dials are adjusted to read 9700 and the MODE is set to CONCENTRATION. This gives a scale expansion of 5 to 6. Then two standard solutions are chosen which have given the nearest absorbance readings lower and higher than the sample. Concentration readings are then taken sequentially in the order, low standard, sample, and high standard, until three values have been obtained for each solution. The averages of each of the three values are calculated and those for the two standards are plotted against the percentages of CaO known to be present from Table 4. A straight line is drawn through the two points and the percentage of CaO in the sample determined from the line. This procedure is repeated for the determination of CaO in each sample of cement which is being analyzed.

Whenever cement standard solutions are being used, NBS certificate values for CaO (corrected for SrO) should be used.

APPENDIX B

Notes on the Use of Plastic Volumetric Equipment

In the use of plastic volumetric apparatus, some unexpected problems were encountered.

1. When using volumetric flasks there was difficulty with stoppering. The flasks, as purchased, came equipped with snap-on polyethylene caps. These, when new, stoppered the flasks tightly. After being used a few times, the caps cracked and then leaked. Extra snap-on caps to fit these flasks seem not to be listed in the catalogs. An inquiry to the manufacturer about the purchase of replacement snap-on caps was met with a shipment of a dozen free new flasks complete with snap-on caps, but no quotation on replacement caps. Hollow standard taper stoppers made of polyethylene are sold by the manufacturer of the flasks. Use of these also presented problems. When used with 50-ml volumetric flasks, these hollow stoppers entrapped solution inside the caps. This entrapped liquid was extremely difficult to dislodge when attempting to mix the solution. With 100-ml and larger flasks, entrapment was not so critical, but still something of a problem.

It was found that the Kimble Glass Company makes solid polyethylene standard taper stoppers that can be used with polypropylene volumetric flasks. Such stoppers were purchased in the sizes for 50-, 100-, 500-, and 1000-ml volumetric flasks. When the solid No. 9 Kimble stoppers were used with 50-ml polypropylene volumetric flasks, all leakage and entrapment problems disappeared. When the No. 13 Kimble stoppers were used with 100-ml flasks, there was leakage from most of the flasks. The Nalgene polyethylene hollow standard taper stoppers could be used with the 100-ml flasks with almost no leakage, and if care was taken to tap the neck of the stoppered flask against the edge of the bench, entrapped liquid could be dislodged. The only way found to keep one 100-ml flask from leaking was to stopper it with a snap-on cap or a size 00 rubber stopper. For 500-ml flasks, the Nalgene hollow standard taper stoppers seemed to fit best. For 1000-ml flasks, the Kimble solid polyethylene stoppers seemed to provide the best closure. Apparently, the user of such flasks must determine for himself the best stopper-flask combination to use.

2. It is difficult to avoid leaving air bubbles at the flask-liquid interface when using polypropylene volumetric flasks. The formation of bubbles can be minimized by cleaning with a good, warm detergent solution followed by rinsing. Then, just before adjusting the level of the solution to the mark, if one tips the stoppered flask, the air space above the liquid can be rolled around the body of the flask to scavenge small bubbles adhering to the inside.

3. Some drops of the solution always seem to adhere to the inside of the neck of the flask above the mark. No way was found in this study to avoid this source of error, except, perhaps, to hope that it would be compensated to some extent, by air bubbles at the flask-liquid interface. This is, admittedly, a source of uncertainty when using polypropylene volumetric flasks.

4. When using polypropylene burets, the same problems persist of having air bubbles at the buret-liquid interface and of having drops of liquid adhering to the inside of the buret above the point at which the buret reading is taken. The problem of bubbles can be almost eliminated by use of two techniques. The buret stand holding the buret can be bounced against the top of the lab bench to cause the bubbles to float upward to the surface. In addition, a clean plastic rod, about the length of the buret, can be moved up and down inside the buret to help dislodge bubbles before letting the solution down to the zero or initial point. After the required volume has been allowed to run out of the buret, it does not seem advisable to use the bouncing or rod techniques. To do so might cause more error than is eliminated. Some uncertainity is certainly associated with using polypropylene burets.

5. When filling a polypropylene buret it is difficult to remove a large air bubble in the buret tip because of the way the buret is constructed. This air bubble can be avoided by placing the empty buret tip, with the stopcock open, in a beaker containing some of the solution, and applying suction from the buret top with a rubber tube which is attached to a water aspirator. After several milliliters of solution have been drawn up into the buret through the tip, the suction is removed, the buret lifted out of the beaker, and the stopcock closed. Then the buret can be filled from the top in the usual manner.

6. Use of polypropylene pipets for aliquoting purposes, appears to be impractical. Few sizes of such pipets are available. Because of drainage and bubble-formation problems encountered in companion plastic ware, there was no attempt in this study to use even [illegible] sizes which are available. Instead, regular glass transfer pipets were used to prepare dilute solutions in this study. To minimize waste of solutions, clean, dry pipets were used unless repeated aliquots of the same solution were to be taken. After a pipet was cleaned and rinsed with distilled water, it was dried by using suction to draw air through it until visual inspection indicated it was dry. The problem of emptying the pipets was considered. Glass transfer pipets are calibrated ordinarily to deliver a specified volume while in contact with a glass surface, not with a polypropylene surface. Some experiments were conducted to see if this presented any problem. Pipets of 1, 4, and 8-ml capacity were calibrated using distilled water and emptying (a) against the neck of a polypropylene flask, and (b) against a glass

stirring rod which had been weighed with the empty flask with which it was used. A summary of triplicate results indicated that an average of 0.0112g more water was delivered by a 1-ml pipet, 0.0035g more was delivered by a 4-ml pipet, and 0.0006g more was delivered by an 8-ml pipet when touching the glass rod as compared to touching the polypropylene flask. The standard deviations in g, using techniques (a) and (b) were 0.0079 and 0.0032 for a 1-ml pipet, 0.0023 and 0.0035 for a 4-ml pipet and 0.0023 and 0.0029 for an 8-ml pipet.

This evidence is not overwhelming, but it was decided to empty pipets against a glass rod for the work which is reported here. When taking an aliquot of a solution, after the pipet was removed from contact with the rod, the latter was then rinsed with distilled water into the flask with which it had been used. Rinsing was not done during the experiments on calibrating the pipets. In that case, the rod was dropped into the flask which was then stoppered and weighed.

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