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U.S. DEPARTMENT OF COMMERCE/National Bureau of Standards

Standard Reference Materials:

Portland Cement Chemical Composition Standards (Blending, Packaging, and Testing)

R. Keith Kirby and Howard M. Kanare

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Portland Cement Chemical Composition Standards (Blending, Packaging, and Testing)

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TABLE OF CONTENTS

LIST OF TABLES

LISTS OF FIGURES

Preface

Standard Reference Materials (SRM's) as defined by the National Bureau of Standards (NBS) are well-characterized materials, produced in quantity and certified for one or more physical or chemical properties. They are used to assure the accuracy and compatibility of measurements throughout the Nation. SRM's are widely used as primary standards in many diverse fields in science, industry, and technology, both within the United States and throughout the world. They are also used extensively in the fields of environmental and clinical analysis. In many applications, traceability of quality control and measurement processes to the national measurement system is carried out through the mechanism and use of SRM's. For many of the Nation's scientists and technologists, it is therefore of more than passing interest to know the details of the measurements made at NBS in arriving at the certified values of the SRM's produced. An NBS series of papers, of which this publication is a member, called the NBS Special Publication - 260 Series, is reserved for this purpose.

The 260 Series is dedicated to the dissemination of information on different phases of the preparation, measurement, certification, and use of NBS SRM's. In general, much more detail will be found in these papers than is generally allowed, or desirable, in scientific journal articles. This enables the user to assess the validity and accuracy of the measurement processes employed, to judge the statistical analysis, and to learn details of techniques and methods utilized for work entailing greatest care and accuracy. These papers also should provide sufficient additional information not found on the certificate so that new applications in diverse fields not foreseen at the time the SRM was originally issued will be sought and found.

Inquiries concerning the technical content of this paper should be directed to the author(s). Other questions concerned with the availability, delivery, price, and so forth, will receive prompt attention from:

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*Send order with remittance to Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20102. Remittance from foreign countries should include an additional one fourth of the purchase price for postage.

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INTRODUCTION

The portland cement Standard Reference Materials (SRMs) are primarily intended for use in the calibration of instrumental methods used in the chemical analysis of commercial portland cements. When necessary, these SRMs can also be used to check the determination of major component concentrations (silica, alumina, calcium oxide, and magnesia) by classical chemical methods.

The National Bureau of Standards (NBS) produced the first portland cement standard (SRM 177) in 1958. To meet the needs of the cement industry's growing use of instrumental methods of analysis, such as x-ray fluorescence and atomic absorption, a series of five standards (SRMs 1011, 1013, 1014, 1015, and 1016) was made available in 1962. When this supply was exhausted, it was replaced by a new series of seven standards (SRMs 633 through 639) which became available in 1973.

A provisional certificate for these seven SRMs was based on a cooperative test program in which 14 laboratories participated, including NBS and the Portland Cement Association (PCA). Although eight of these laboratories used "wet chemistry" for the major constituents (NBS measurements were made by x-ray fluorescence), none of the tests achieved the measurement precision achieved by NBS and PCA on the previous series of five SRMs. Accordingly, in 1974 NBS placed a contract with PCA to perform, with the aid and consultation of the Erlin, Hine Associates, a "definitive analyses" of the seven standards. These analyses resulted in the final certification in 1977.

In 1981 a questionnaire was distributed by the American Society for Testing and Materials (ASTM) to the members of its committee on cement, ASTM Committee C-1, to solicit suggestions for the chemical composition of two new SRMs. The majority of nearly 50 responses to the questionnaire indicated that there was a need to fill in some blank areas in the ranges for some constituents, such as SO_3, and to extend the range for some constituents, such as K_2O. Under contract to NBS, the PCA proceeded to obtain, blend, package, and analyze these standards. Subsequently, SRMs 1880 and 1881 were certified in 1982 and 1983, respectively.

The purpose of this paper is to present a detailed description of the blending, packaging, testing, and characterization of the portland cement SRMs.

SRMs 177, 1011, 1013, 1014, 1015, and 1016

While most of the information on these standards was not fully documented, the following facts are known: The cements were selected on the basis of analyses conducted at NBS by B. Leonard Bean of the Inorganic Building Materials Section and were packaged in essentially the same manner as at present--i.e., the samples were placed in stoppered glass vials and then flame sealed in outer glass vials. Each of these standards took several days to vial with the possible result that the water content may have changed between the initial and final vialed units due to changes in the ambient relative humidity. This may have caused the larger-than-usual variation of the loss-on-ignition values.

Cooperative testing programs provided the data for certification. In the case for SRM 177, thirteen laboratories provided the analyses while ten laboratories provided analyses in the "1000 series". In all cases, average values for the concentration of the constituents were used for the certification, but only after a careful technical and statistical analysis eliminated some values. It is interesting to note that the certificates for the "1000 series" SRMs were "provisional" which meant that there may have been some doubt about the average values.

Figure 1 presents values for many of the constituents of the portland cement standards. Copies of the certificates are shown in Appendix A.

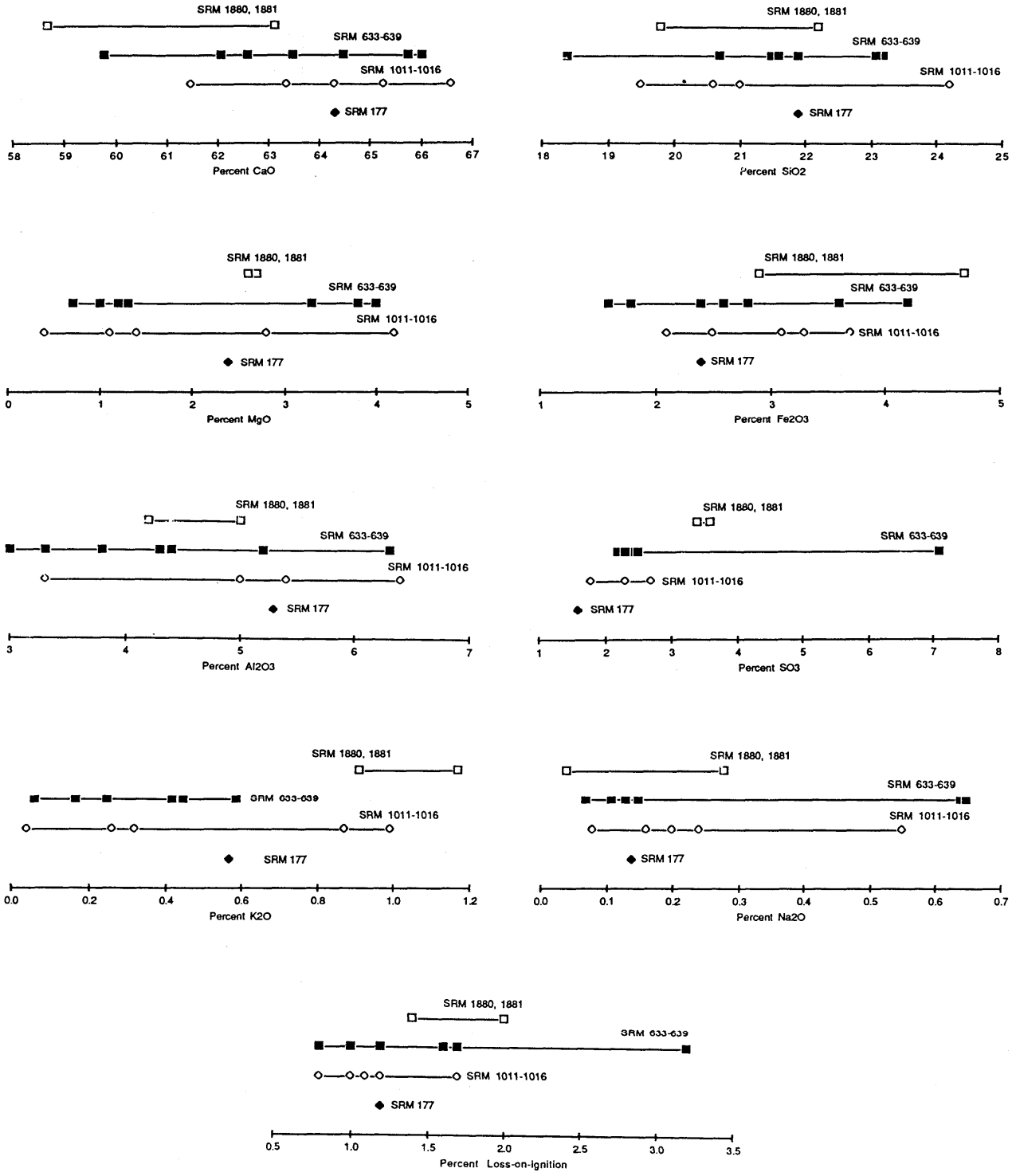

Figure 1. Relative values for many of the constituents of SRMs 177, 1011, 1013 through 1016, 633 through 639, 1880, and 1881.

SRMs 633 THROUGH 639

With the approaching depletion of stock of the "1000 series", it became necessary to select cements for the replacement series of standards. Accordingly, a letter was sent to all cement producers requesting information on the chemical composition of portland cements currently being produced. Response to this letter was favorable but unfortunately either most of the plants had no information on minor constituents or in some cases the information supplied was unreliable. The information was sufficient, however, to allow Bruce Foster of the NBS Cement and Concrete Research Laboratory to select seven cements, see Table 1, including an expansive type portland cement. White cements were ruled out because of their virtual absence of iron.

Table 1. Portland Cement SRMs Percent by Weight

SRM	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	SrO	TiO_2	K_2O	Na_2O	Loss
177	64.2	21.9	5.3	2.4	1.6	2.4	0.2	0.3	0.6	0.1	1.2
1011	66.6	21.0	5.4	2.1	1.8	1.1	0.1	0.2	0.3	0.1	1.1
1013	64.3	24.2	3.3	3.1	1.8	1.4	0.1	0.2	0.3	0.2	1.0
1014	63.4	19.5	6.4	2.5	2.7	2.8	0.3	0.2	1.0	0.2	0.8
1015	61.5	20.6	5.0	3.3	2.3	4.2	0.1	0.3	0.9	0.2	1.7
1016	65.3	21.0	5.0	3.7	2.3	0.4	0.2	0.3	0.0	0.6	1.2
633	64.5	21.9	3.8	4.2	2.2	1.0	0.3	0.2	0.2	0.6	0.8
634	62.6	20.7	5.2	2.8	2.2	3.3	0.1	0.3	0.4	0.2	1.6
635	59.8	18.4	6.3	2.6	7.1	1.2	0.2	0.3	0.4	0.1	3.2
636	63.5	23.2	3.0	1.6	2.3	4.0	0.0	0.2	0.6	0.1	1.2
637	66.0	23.1	3.3	1.8	2.4	0.7	0.1	0.2	0.2	0.2	1.7
638	62.1	21.5	4.4	3.6	2.3	3.8	0.1	0.2	0.6	0.1	1.0
639	65.8	21.6	4.3	2.4	2.5	1.3	0.2	0.3	0.1	0.6	1.0
1880	63.1	19.8	5.0	2.9	3.4	2.7	0.1	0.2	0.9	0.3	1.4
1881	58.7	22.2	4.2	4.7	3.6	2.6	0.1	0.2	1.2	0.0	2.0

Three 94-lb bags of each cement were donated by the producers. Upon receipt, the three bags of cement were sifted through a No. 50 wire-cloth sieve to remove oversize particles and to break up conglomerates (see Figure 2). The cement was then placed in a 4 cubic-foot double-cone blender (see Figure 3) and mixed for four hours. The cement was then scooped from the blender into plastic bags so that all of the bags contained representative samples of the mixed cement. The bags were than placed in containers which were sealed and set aside until the cement was packaged in vials.

Figure 2.

Sieving one of the "600 series" portland cements.

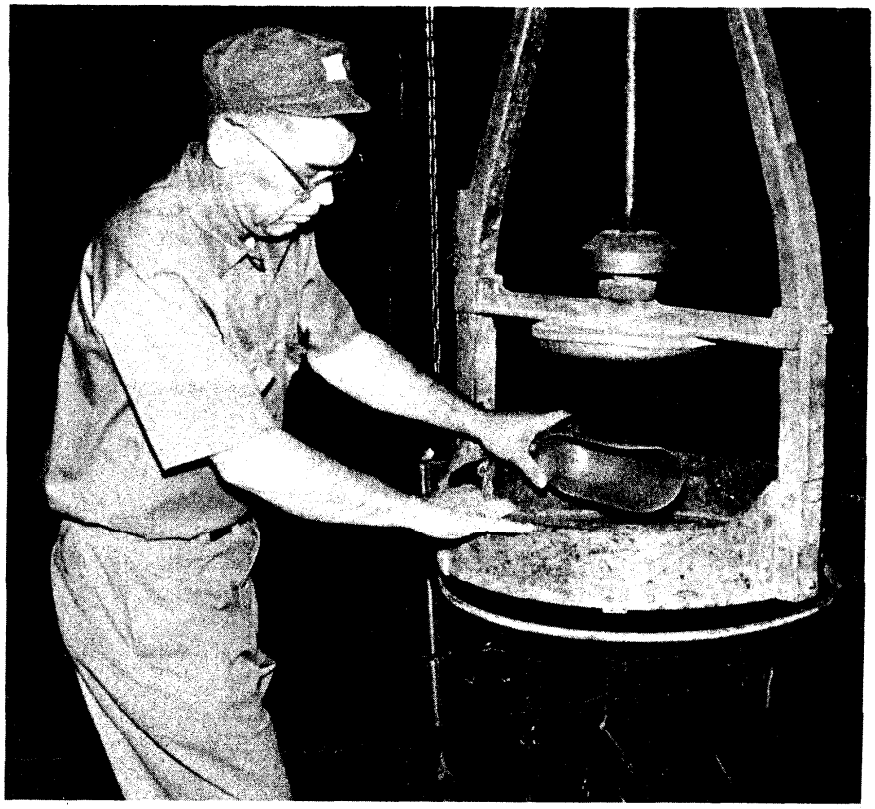

Figure 3.

Blending one of the "600 series" portland cements.

Rather than fill the vials one at a time, as in the past, a technique was developed in which about 400 vials were placed in a tray (see Figure 4) filled with cement, vibrated to settle the cement, and capped (see Figure 5.)

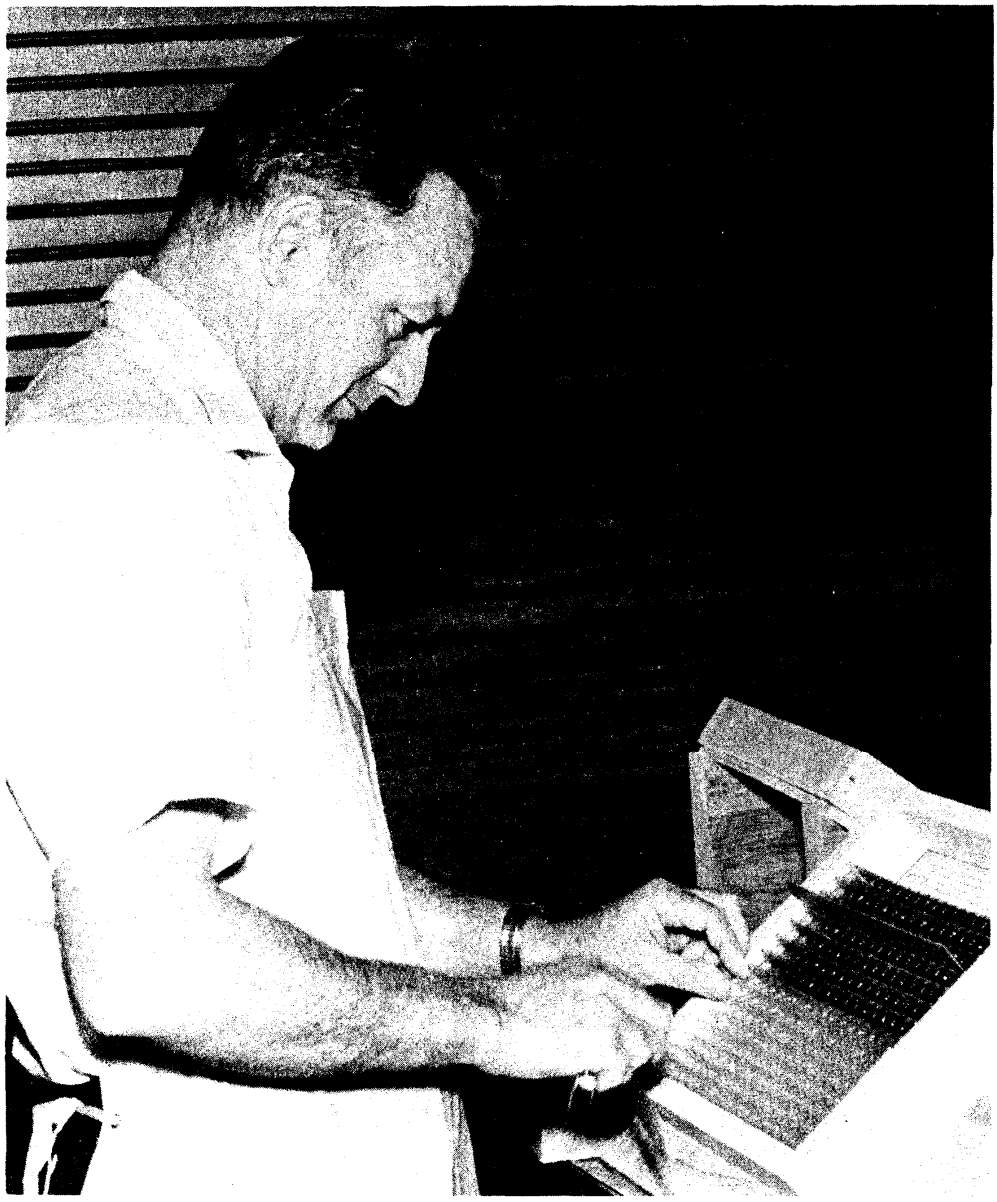

Figure 4. Placing vials in a tray before filling with cement.

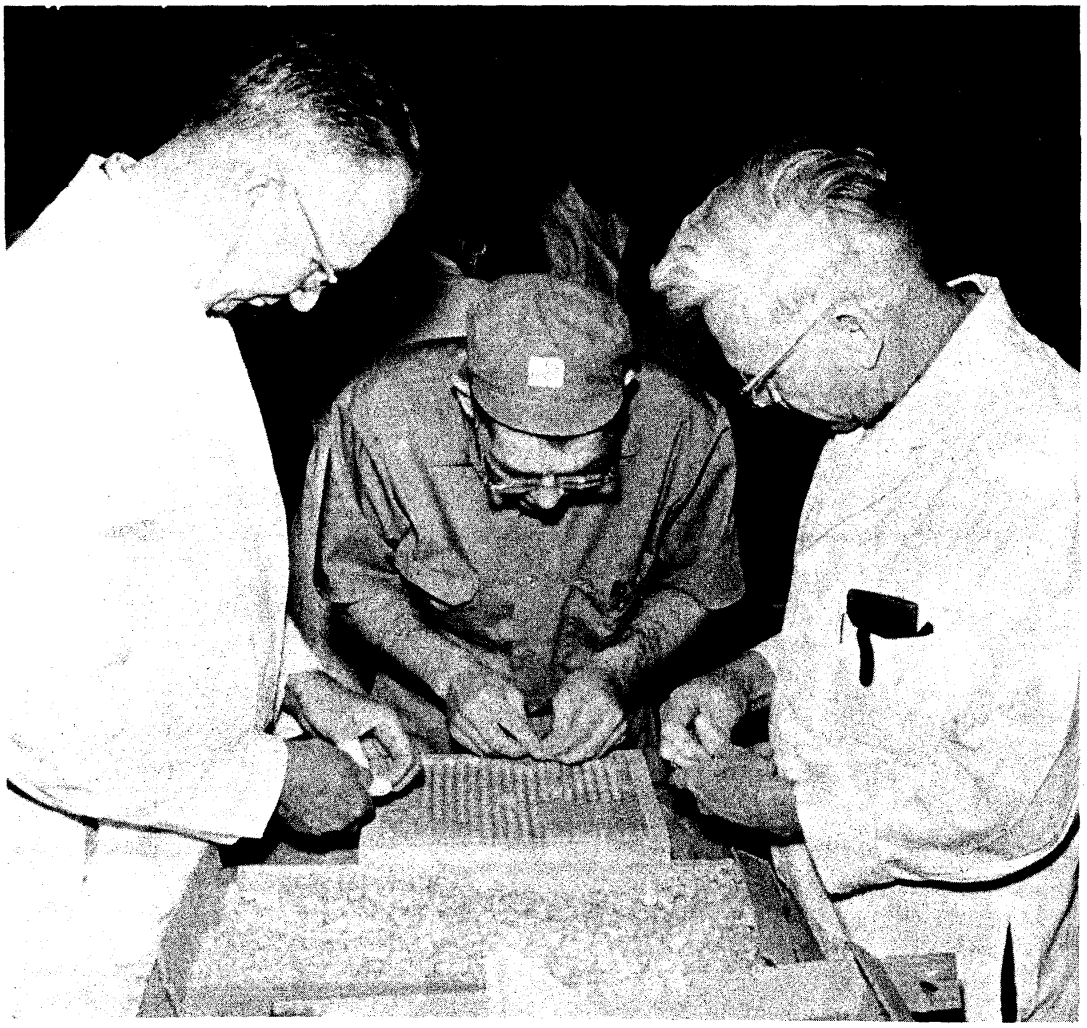

Figure 5. Capping filled vials.

Using this technique, the cement for one of the standards could be packaged in one day. Packaging was carried out in February when the humidity was low. The filled and capped vials were stored in 15 or 16 sealed cans until they could be flame-sealed in the outer glass vials. Flame sealing was accomplished with the automatic sealer shown in Figure 6.

The homogeneity of each standard was tested by comparing the calcium and sulfur variation between two vials taken from each of the containers. The 32 specimens were prepared by briquetting and were then analyzed (repeating each measurement four times) by normal x-ray fluorescence methods. The data obtained in these tests are given in Appendix B and are summarized in Table 2. The data indicate that each of the cement standards was sufficiently homogeneous. The reason for measuring the variations of the calcium and sulfur content is that in the production of portland cement, gypsum (which contains most of the sulfur) is added to and ground with the cement clinker (which contains calcium, the most abundant element) to help control the setting time of the concrete. Therefore, if these elements are homogeneously distributed in the standards, it is a good indication that the mixing was complete and that the other constituents are also uniformly distributed.

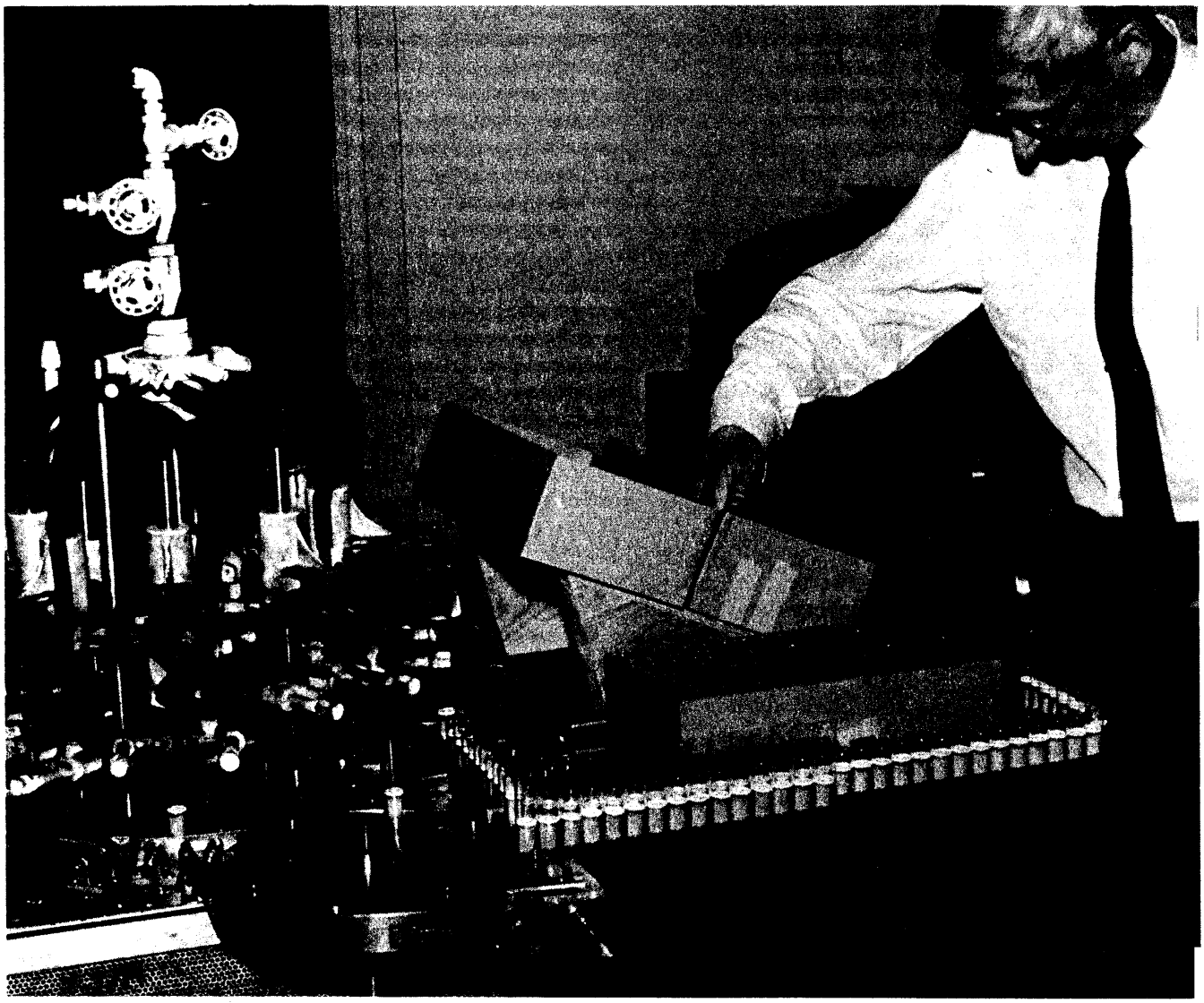

Figure 6. Flame sealing the outer glass vials.

As with the earlier SRMs, a cooperative test program was set up involving NBS, PCA, the Army Corps of Engineers, and ten cement manufactures. These 13 laboratories are listed in Appendix C along with a comparative summary of their results prepared by William G. Hine*. The methods used were primarily instrumental with the "1000 series" used for calibration. Only two laboratories performed wet analytical procedures that were considered to be reasonably accurate, according to and using methods specified in ASTM C114, Standard Methods for Chemical Analysis of Hydraulic Cement [1]. Even in these

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tests, however, corrections were not made for incomplete separations. Five other laboratories used short-cut modifications of the ASTM standard methods. One laboratory used the Jugovic [2] method which is a combination of colorimetric and complexometric methods in which the samples are fused with sodium hydroxide and then dissolved in hydrochloric acid. Seven laboratories, including NBS, used x-ray fluorescence techniques in which all but one used pelletized samples. That laboratory fused the cements with lithium borate. Two laboratories used atomic absorption techniques in which the cements are fused with lithium metaborate and then dissolved in nitric acid [3].

Table 2. Results of the Homogeneity Tests on the "600 Series" SRMs

		CaO		SO_3	
SRM	n	Std Dev	Coef of Var	Std Dev	Coef of Var
633	32	0.069% by wt.	0.105%	0.015% by wt.	0.67%
634	32	0.057	0.091	0.012	0.56
635	32	0.094	0.158	0.028	0.40
636	30	0.111	0.176	0.019	0.82
637	30	0.085	0.129	0.011	0.47
638	30	0.077	0.124	0.016	0.68
639	29	0.115	0.175	0.020	0.79

The results of this cooperative test program were used for the "provisional" certification of the "600 series" in 1974 (see Appendix C). More than 3000 individual determinations were reported for the constituents in the seven SRMs. The certified values were obtained by a critical evaluation of the analytical methods and the reported data. Because the results of this test program did not provide the accuracy necessary to meet the needs of an ASTM method of analysis, NBS contracted with PCA (with William G. Hine acting as consultant) to provide for the "definitive analyses" of these SRMs. For this work, wet chemistry techniques were used to provide the basic measurement of the major components and instrumental techniques were used not only to measure the lesser components but to also determine impurity levels in the precipitates and filtrates to provide corrections for the wet chemistry results.

In general, x-ray fluorescence (XRF) and atomic absorption spectroscopy (AAS) techniques were used. The particular XRF employed allowed detection of elements of atomic number 12 (magnesium) and above with greatly varying sensitivity. Limited experimentation with various precipitates indicated the detection limits to range from 0.4 milligram for magnesium oxide (equivalent to 0.08 percent in the SRM), to 0.2 milligram for silica (0.04 percent), to less than 0.01 milligram (0.02 percent) for elements of the fourth period of the Periodic Table of Elements.

AAS was employed where the sensitivity of this technique allowed detection of 0.1 milligram (0.02 percent) of a constituent. Analyses for sodium and potassium, for example, were frequently made by this technique. Because of its suitability for analyzing liquids, AAS was also used to examine the filtrates from each precipitation step. By the use of standard addition techniques, it was demonstrated that a sensitivity of 0.1 milligram (0.02 percent) was achievable for the analyzed elements.

Finally, optical emission spectroscopy (capable of detecting elements in the parts per million or less level) was employed in a few instances (e.g., the ammonium hydroxide group precipitate of SRM 635). This method was used as check on the XRF results.

GENERAL ANALYTICAL TECHNIQUES

The scheme of the analytical program is shown in Figure 7. A 0.5-g sample was used in all cases. Newly opened vials of the SRM were used for determinations of all the major components. For minor components, previously opened vials were occasionally used.

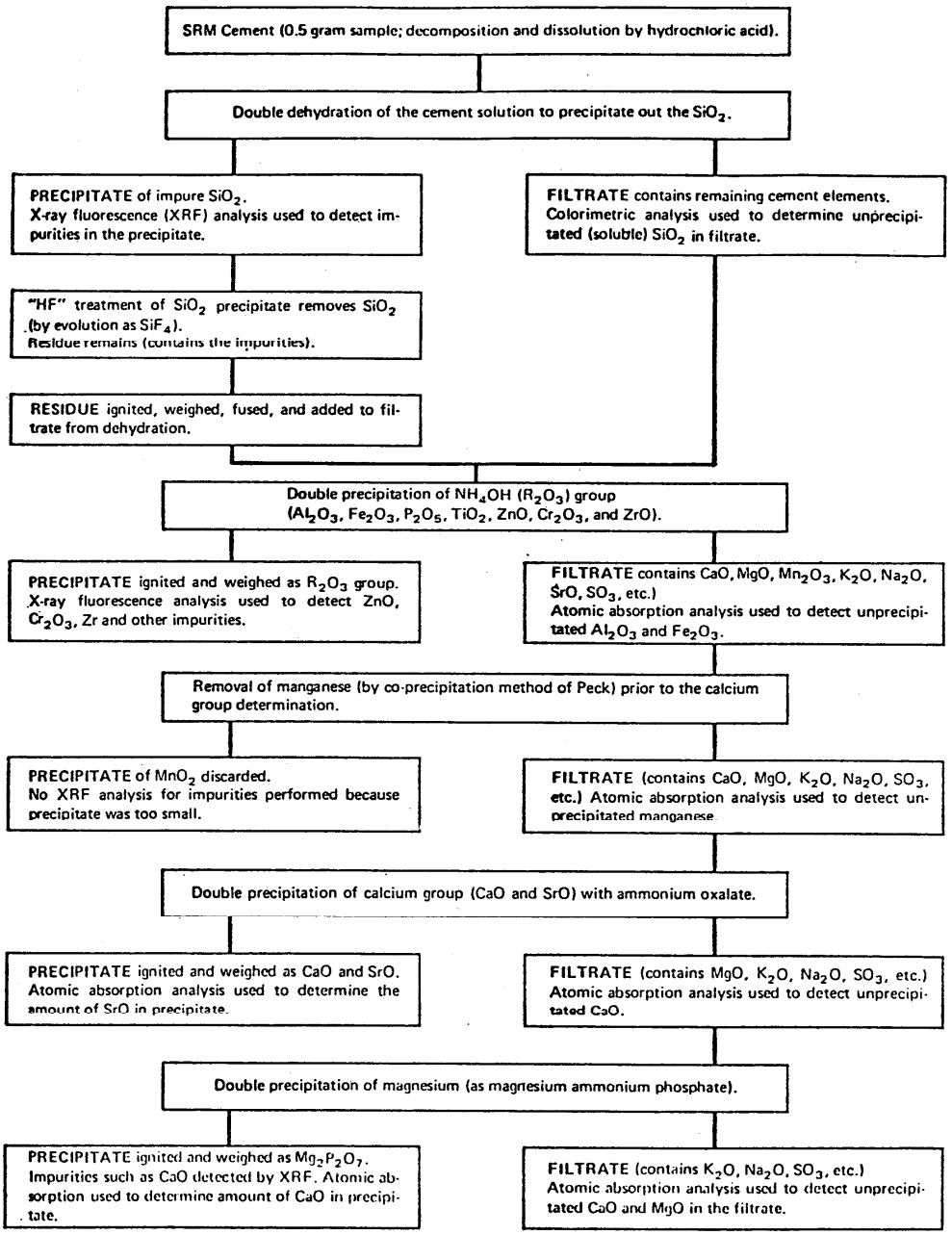

Figure 7. Flow sheet for the analyses of the "600 series" SRMs.

Silica

SiO_2 was determined by classical double dehydration techniques given in the ASTM C114 method. After dissolution of the sample, silicic acid is dehydrated by fuming with an appropriate acid. The solution is filtered and the silica is ignited, weighed, and then volatilized with hydrofluoric acid (HF). The residue is ignited and weighed; the loss in weight represents silica. The results of these analyses are presented in Table 3. Because the substances remaining after "HF" treatment are re-introduced into the filtrate from the silica precipitate, and since silica is determined by "difference", contaminants have little or no effect on the analysis. Nevertheless, two sets of silica precipitates were examined qualitatively by XRF techniques. Aluminum, chromium, iron, and titanium were detected in some precipitates. No significant error is apparent resulting from these contaminants.

The presence of small amounts of fluoride (less than about 0.3 percent) or boron (less than 0.1 percent) will not cause significant errors by volatilization during ignition of the silica precipitate prior to "HF" treatment. Since these SRMs contain 0.08 percent or less of fluoride and less than 0.01 percent boron, very little error is likely to result.

Table 3. Results of the Analyses of SiO_2, % by wt.

	Gravimetric			AAS		
SRM	Average	n	Std Dev	Average	n	Std Dev
633	21.88	7	0.023	21.88	5	0.062
634	20.73	8	0.024	20.79	5	0.091
635	18.41	9	0.030	18.37	5	0.065
636	23.22	10	0.024	23.29	5	0.078
637	23.07	9	0.046	23.09	5	0.078
638	21.48	7	0.035	21.51	5	0.049
639	21.61	7	0.034	21.63	5	0.116

An extensive analytical program to detect and quantitate silica remaining in the filtrate was undertaken using procedures based on the "molybdenum blue" method. In every case, the optical absorbance of the sample "blank" solution was at least three fourths of that of the sample indicating that the amount of silica unprecipitated is less than 0.02 percent.

XRF analyses of the ammonium hydroxide ("R_2O_3") group precipitate, and of the calcium and magnesium precipitates, did not detect silica at a detection limit of 0.04 percent.

Atomic absorption results, also shown in Table 3, are in good agreement with the gravimetric data.

"R_2O_3" Group (Aluminum, Iron, Phosphorus, Titanium, Chromium and Zinc)

The combined group, "R_2O_3", was determined by the classical double precipitation method given in ASTM C114 using ammonium hydroxide as precipitant--followed by ignition to convert all elements to the oxide form.

The solutions from the silica determination, after combining with residue from the "HF" volatilization step, were used for this analysis. The data are given in Table 4.

Table 4. Results of the Analyses of the "R_2O_3" Group, % by wt.

SRM	Average	n	Std Dev
633	8.47	3	0.076
634	8.54	3	0.053
635	9.40	4	0.043
636	4.92	4	0.071
637	5.55	4	0.062
638	8.42	3	0.053
639	7.09	3	0.023

Two sets of mixed oxide precipitates were analyzed by XRF spectroscopy. The group members aluminum, iron, titanium, zinc, and chromium, were detected in all the specimens. Zirconium was detected in six of the samples; calcium in two, and nickel possibly in one. Phosphorus is known to be present in all the precipitates, but analysis for it was not carried out.

Using standard addition techniques, reanalysis by XRF indicated that the quantities of nickel present were less than 0.01 percent. Using AAS procedures, and standards prepared to contain amounts of iron and aluminum approximately equal to those in the sample, the amounts of calcium, magnesium, potassium, and sodium oxides in the precipitates were found to be less than 0.01 percent.

Because of questionable aluminum data for SRM 635 (to be discussed later), the precipitate for this sample was also analyzed by optical emission spectrographic methods. The only impurity of consequence was silicon. However, since the soluble silica data revealed no unusual amounts of silica in the solution from the silica removal step, this interference is small (0.02 percent or less).

One set of filtrates from the "R_2O_3" group precipitate step was analyzed by AAS methods for aluminum and iron. These elements were not detected in the filtrate - indicating complete precipitation.

Iron Oxide

Fe_2O_3 was determined on separate samples by the volumetric titration method given in ASTM C114 standard methods of analysis. These data are given in Table 5. The values reported are verified by the AAS data. It is noted that both methods give similar results.

Table 5. Results of the Analyses of Fe_2O_3, % by wt.

	Volumetric			AAS		
SRM	Average	n	Std Dev	Average	n	Std Dev
633	4.20	3	0.006	4.25	5	0.019
634	2.84	3	0.010	2.87	5	0.022
635	2.61	3	0.012	2.63	5	0.017
636	1.61	3	0.006	1.62	5	0.011
637	1.80	3	0.006	1.81	5	0.015
638	3.55	3	0.000	3.58	5	0.030
639	2.40	3	0.000	2.40	5	0.016

Titania

TiO_2 was determined on separate samples by a colorimetric method using Tiron reagent, as developed by others and refined for cement by Jugovic. The data are given in Table 6. The Tiron method is more sensitive than the classical peroxide method given in ASTM C114.

Table 6. Results of the Analyses of TiO_2, % by wt.

SRM	Average	n	Std Dev
633	0.238	3	0.003
634	0.293	3	0.004
635	0.319	3	0.006
636	0.178	3	0.006
637	0.210	3	0.005
638	0.252	3	0.004
639	0.316	3	0.003

Phosphorus Oxide

P_2O_5 was determined on separate samples by the "molybdenum blue" colorimetric method given in the ASTM standard method. The data are given in Table 7.

Table 7. Results of the Analyses of P_2O_5, % by wt.

SRM	Average	n	Std Dev
633	0.238	3	0.002
634	0.095	3	0.001
635	0.169	3	0.001
636	0.084	3	0.001
637	0.244	3	0.001
638	0.062	3	0.001
639	0.082	3	0.001

Zinc Oxide

ZnO was determined on separate samples by AAS, using a standard addition technique [4]. The values are given in Table 8.

Table 8. Results of the Analyses of ZnO, % by wt.

SRM	Average	n	Std Dev
633	0.005	1	-
634	0.024	1	-
635	0.007	1	-
636	0.027	1	-
637	0.012	1	-
638	0.095	2	0.007
639	0.007	1	-

Chromium Oxide

Cr_2O_3 was determined on separate samples by AAS, using a standard addition technique [4]. The data are given in Table 9.

Table 9. Results of the Analyses of Cr_2O_3, % by wt.

SRM	Average	n	Std Dev
633	0.008	2	0.001
634	0.076	2	0.001
635	0.005	2	0.000
636	0.006	2	0.001
637	0.010	2	0.001
638	0.010	2	0.000
639	0.005	2	0.000

Alumina

Al_2O_3 was determined by difference ("R_2O_3" percent minus "X_2O_3" percent), subtracting the amounts of iron, titanium, phosphorus, zinc, and chromium oxides from the ammonium hydroxide group total. The data are given in Table 10. Alumina was also determined by AAS and the values are in good agreement (generally within 0.02 percent) except for SRM 635 which differs by 0.16 percent.

Table 10. Results of the Analyses of Al_2O_3, % by wt.

Determination by Difference					AAS		
SRM	"R_2O_3"	"X_2O_3"	Al_2O_3	Std Dev	Average	n	Std Dev
633	8.47	4.69	3.78	0.062	3.79	5	0.029
634	8.54	3.33	5.21	0.044	5.18	5	0.044
635	9.40	3.11	6.29	0.038	6.13	5	0.052
636	4.92	1.90	3.02	0.062	3.07	5	0.029
637	5.55	2.27	3.28	0.054	3.24	5	0.015
638	8.42	3.97	4.45	0.044	4.48	5	0.026
639	7.09	2.81	4.28	0.019	4.29	5	0.023

An extensive analytical program was carried out to determine a cause for this large difference. Several "R_2O_3" precipitates for this sample were analyzed by XRF spectroscopy in the hope of disclosing previously undetected components. None were detected. Similar analyses were made by optical emission spectroscopy. In this case, other elements were detected--boron, vanadium, copper, lead, tin, nickel, molybdenum, and silver. However, the amount of each of these elements present was much less than 0.01 percent.

The possibility of interference in either gravimetric or atomic absorption methods by the large amounts of sulfate exists, but experiments designed to determine the effect of sulfate on the atomic absorption intensities for aluminum failed to disclose significant interference.

Manganese Oxide

Mn_2O_3 was determined on separate samples by AAS. The data are given in Table 11. Experience indicates that the atomic absorption analysis for manganese in cement is much more precise and accurate than that given by the method in ASTM C114.

Prior to the calcium group determination, manganese was not removed by the usual bromine oxidation procedure because it was found that substantial amounts of manganese (particularly in SRM 635) remained in solution until the calcium precipitation step. When this manganese was detected in the calcium oxide precipitate, a search was made for a more quantitative method for its removal. The coprecipitation (or zirconium collector) method of Peck [5] was found to be excellent, and was used for succeeding analyses. The method removes the manganese prior to the calcium determination step by coprecipitating it with zirconium hydroxide.

Manganese separated by the method of Peck was determined by dissolution and quantitation by AAS using pure manganese standards. The results are also listed in Table 11. These data show that only a small amount of manganese is lost by the Peck procedure. Some is undoubtedly entrapped in the mixed oxide group ("R_2O_3") precipitate and some remains unprecipitated until the calcium or magnesium steps.

Table 11. Results of the Analyses of Mn_2O_3, % by wt.

	Separate Samples			Recovered Samples		
SRM	Average	n	Std Dev	Average	n	Std Dev
633	0.04	3	0.006	0.03	2	0.000
634	0.28	3	0.006	0.26	2	0.028
635	0.09	3	0.000	0.07	4	0.017
636	0.12	3	0.006	0.11	3	0.000
637	0.06	3	0.000	0.04	4	0.006
638	0.05	3	0.000	0.04	4	0.006
639	0.08	3	0.006	0.07	4	0.000

Calcium Group

CaO (+ SrO) was determined by the classical double precipitation method employing oxalate. Most of the strontium is also precipitated in this procedure, and the term "calcium group" is applied. The results are given in Table 12.

Table 12. Results of the Analyses of Calcium Group, % by wt.

SRM	Average	n	Std Dev
633	64.75	6	0.047
634	62.65	5	0.072
635	59.98	6	0.047
636	63.53	8	0.057
637	66.10	5	0.126
638	62.11	5	0.087
639	65.85	6	0.072

Analyses of the calcium group precipitate, after removal of manganese by the Peck method, were made by XRF spectroscopy. No manganese was found in the precipitates.

The filtrate from the calcium group precipitation step was analyzed for calcium by AAS. Calcium was detected, but because of the large amounts of ammonium salts, quantitative analysis could not be easily made. However, since calcium appeared in the magnesium precipitate, analysis of the latter was chosen as the more suitable method for determining the unprecipitated calcium.

Strontium Oxide

SrO was determined on separate samples by the use of AAS. The date are given in Table 13. There is no ASTM C114 method for the determination of strontium. The ignited oxide precipitates of the calcium group were dissolved in acid and strontium determined by AAs using standards containing approximately equivalent amounts of calcium and acid. The data, also given in Table 13, suggest that

the calcium group precipitation step is not quantitative for SrO.

Table 13. Results of the Analyses of SrO, % by wt.

	Separate Samples			CaO Precipitate		
SRM	Average	n	Std Dev	Average	n	Std Dev
633	0.31	3	0.006	0.28	4	0.013
634	0.12	3	0.010	0.11	4	0.008
635	0.21	3	0.010	0.18	4	0.006
636	0.04	3	0.000	0.04	5	0.000
637	0.09	3	0.006	0.08	4	0.005
638	0.07	3	0.006	0.06	4	0.010
639	0.15	3	0.006	0.12	4	0.015

Magnesia

MgO was determined by the classical double precipitation method using ammonium phosphate, with ignition to the pyrophosphate. The analytical data are given in Table 14. It is noted that these values are useful for comparison with ASTM C114 results. However, the inclusion of calcium in the precipitate (as noted above) causes these data to be slightly erroneous.

The magnesium oxide precipitates were analyzed by XRF spectroscopy. Small amounts of calcium were detected in each. The precipitates were dissolved in acid and analyzed by AAS, using standard solutions containing approximately equivalent amounts of magnesium and acid. The amounts of calcium determined (0.02 to 0.04 percent) were used to correct both the calcium and magnesium values.

The percent of CaO in MgO in Table 15 must be multiplied by the appropriate conversion factor (0.6674) before it is used for correcting the MgO value in Table 14. The reason for this is as follows: Calcium occurs in the $Mg_2P_2O_7$ precipitate as calcium phosphate, $Ca_3(PO_4)_2$. The weight of calcium oxide in the $Mg_2P_2O_7$ (as determined by AAS) is multiplied by 1.8437. This value is subtracted from the weight of $Mg_2P_2O_7$ before the percent MgO is calculated. The factor 1.8437 is obtained by dividing the molecular weight of $Ca_3(PO_4)_2$ by 3 times the molecular weight of calcium oxide.

The filtrate from the magnesium precipitation step was analyzed by AAS for calcium and magnesium. While neither was detected, the severe interference of large amounts of ammonium ion in the filtrate makes this determination uncertain.

Table 14. Results of the Analyses of MgO, % by wt.

	Gravimetric			CaO in		AAS		
SRM	Average	n	Std Dev	MgO	Difference	Average	n	Std Dev
633	1.06	4	0.026	0.02	1.04	1.07	5	0.012
634	3.33	5	0.023	0.03	3.30	3.39	5	0.022
635	1.26	3	0.053	0.03	1.23	1.28	5	0.011
636	3.98	6	0.035	0.03	3.95	3.99	5	0.020
637	0.68	3	0.031	0.01	0.67	0.71	5	0.004
638	3.86	5	0.059	0.03	3.83	3.88	5	0.030
639	1.28	5	0.030	0.02	1.26	1.30	5	0.007

AAS data are also given in Table 14 for comparison purposes. The results obtained are slightly higher than the corrected gravimetric results. The reason for this difference is not known for certain, but may be due to small positive errors in the MgO certified values of the "1000 series" SRMs which were used to prepare the AAS calibration curves.

Calcium Oxide

CaO was determined by "difference" (calcium group minus the strontium determined in the group precipitates). To this net calcium oxide must be added the amount that was unprecipitated. Fortunately, it is coprecipitated with magnesium, and can be determined. This determination was discussed above under the magnesium oxide determination. However, this correction is not made during an ASTM C114 referee analysis, and thus for comparative purposes, "uncorrected" data, as well as corrected data need to be reported. These data are given in Table 15 along with the calcium oxide values determined by AAS. These values agree with the corrected CaO values.

Table 15. Results of the Analyses of CaO, % by wt.

		SrO +	Uncor- rected	CaO in			AAS		
SRM	CaO	SrO	CaO	MgO	CaO	Std Dev	Average	n	Std Dev
633	64.75	0.28	64.47	0.03	64.50	0.044	64.53	5	0.14
634	62.65	0.11	62.54	0.04	62.58	0.065	62.70	5	0.14
635	59.98	0.19	59.79	0.04	59.83	0.043	59.77	5	0.11
636	63.53	0.04	63.49	0.05	63.54	0.050	63.57	5	0.16
637	66.10	0.08	66.02	0.02	66.04	0.113	66.05	4	0.14
638	62.11	0.06	62.05	0.04	62.09	0.078	62.08	5	0.12
639	65.85	0.12	65.73	0.03	65.76	0.067	65.70	5	0.10

Sulfur Trioxide

SO_3 was determined on separate samples by ASTM C114 referee method (using a precipitation with barium chloride) and as total sulfur (using an induction furnace to evolve sulfur oxides, which were determined by titration). These results are listed in Table 16.

Since silica and iron are reported to cause interference under certain circumstances with the determination of SO_3, a procedure in which most of the silica and the ammonium hydroxide group elements were removed (either by dehydration or by precipitation with ammonia) was used before precipitation of sulfur as barium sulfate.

The agreement of results between the gravimetric and the total sulfur, except for SRM 635, indicates that no significant sulfide sulfur exists in the SRMs. An ASTM C114 sulfide determination was made on SRM 635 and none was found.

Table 16. Results of the Analyses of SO_3, % by wt.

SRM	Average	n	Std Dev	Average	n	Std Dev
633	2.20	2	0.000	2.20	3	0.046
634	2.21	2	0.028	2.18	3	0.012
635	7.07	2	0.028	7.23	3	0.115
636	2.31	2	0.000	2.30	2	0.042
637	2.38	2	0.014	2.40	2	0.021
638	2.34	2	0.021	2.37	2	0.014
639	2.48	2	0.021	2.46	2	0.000

Potassium and Sodium Oxides

These alkalies were determined on separate samples by AAS. The results are given in Tables 17 and 18. Atomic absorption was selected as a matter of convenience. This method and flame photometry, as designated in ASTM C114, should give comparable results.

Table 17. Results of the Analyses of K_2O, % by wt.

SRM	Average	n	Std Dev
633	0.17	5	0.000
634	0.42	5	0.007
635	0.45	5	0.004
636	0.59	5	0.009
637	0.25	5	0.005
638	0.59	5	0.005
639	0.06	5	0.000

Table 18. Results of the Analyses of Na_2O, % by wt.

SRM	Average	n	Std Dev
633	0.64	5	0.010
634	0.15	5	0.005
635	0.07	5	0.005
636	0.11	5	0.004
637	0.15	5	0.004
638	0.13	5	0.004
639	0.65	5	0.004

Fluoride

Fluorine (as fluoride ion) was determined on separate samples by an ion-selective electrode procedure developed at PCA by W.F. Mivelaz [6], in which a calomel reference electrode, a specific ion meter, and two standard fluoride solutions (0.01 and 0.10 percent fluorine) are used. In this procedure, the sample is dissolved in an acidified alum solution and the fluoride ion is freed by the addition of sodium citrate which complexes the aluminum. The results are given in Table 19.

Table 19. Results of the Analyses of Fluoride, % by wt.

SRM	Average	n	Std Dev
633	0.08	4	0.000
634	0.08	4	0.006
635	0.04	4	0.006
636	0.06	4	0.006
637	0.04	4	0.005
638	0.04	4	0.005
639	0.02	3	0.000

To determine if boron would interfere, known amounts of boric acid were introduced into some samples. No interference was observed.

Miscellaneous Element

Determinations of barium, boron, chloride, and zirconium were made on separate samples. All were less than 0.01 percent.

Ignition Loss

Loss-on-ignition (1000 ^{o}C for 30 minutes) was determined on separate samples using the ASTM C114 method. The data are given in Table 20.

Table 20. Results of the Analyses of Ignition Loss, % by wt.

SRM	Average	n	Std Dev
633	0.75	3	0.006
634	1.62	3	0.036
635	3.24	3	0.017
636	1.16	3	0.026
637	1.69	3	0.055
638	0.95	3	0.036
639	1.00	3	0.025

Summary

The results of all analyses are given in Table 21 along with the pooled standard deviations for the seven cements. These pooled standard deviations were determined as

$$s_p^2 = \frac{\Sigma(n_i-1)s_i^2}{\Sigma(n_i-1)}$$

where it was assumed that the precision was the same for all of the cements. These results formed the basis for the certification of SRMs 633 through 639.

Table 21. Final Results for the "600 Series" SRMs, % by wt.

Component	SRM							S_p
	633	634	635	636	637	638	639	
CaO	64.50	62.58	59.83	63.54	66.04	62.09	65.76	0.07
SiO_2	21.88	20.73	18.41	23.22	23.07	21.48	21.61	0.03
Al_2O_3	3.78	5.21	6.29	3.02	3.28	4.45	4.28	0.06
Fe_2O_3	4.20	2.84	2.61	1.61	1.80	3.55	2.40	0.01
SO_3	2.20	2.21	7.07	2.31	2.38	2.34	2.48	0.02
MgO	1.04	3.30	1.23	3.95	0.67	3.83	1.26	0.04
K_2O	0.17	0.42	0.45	0.59	0.25	0.59	0.06	0.01
TiO_2	0.24	0.29	0.32	0.18	0.21	0.25	0.32	0.01
Na_2O	0.64	0.15	0.07	0.11	0.15	0.13	0.65	0.01
SrO	0.31	0.12	0.21	0.04	0.09	0.07	0.15	0.01
P_2O_5	0.24	0.10	0.17	0.08	0.24	0.06	0.08	<0.01
Mn_2O_3	0.04	0.28	0.09	0.12	0.06	0.05	0.08	0.01
F	0.08	0.08	0.04	0.06	0.04	0.04	0.02	0.01
ZnO	0.01	0.02	0.01	0.03	0.01	0.10	0.01	<0.01
Cr_2O_3	0.01	0.08	0.01	0.01	0.01	0.01	0.01	<0.01
Ign Loss	0.75	1.62	3.24	1.16	1.69	0.95	1.00	0.04
Total	100.1	100.0	100.0	100.0	100.0	100.0	100.2	

S_p is the pooled standard deviation for the seven SRMs.

SRMs 1880 and 1881

It became apparent that for the portland cement SRMs to be more useful to the cement industry in calibrating instrumental methods, some new standards should be certified with compositions that either filled in some blank areas in the composition ranges or extended them (see Figure 1). Accordingly, a questionnaire was distributed to members of ASTM Committee C-1 on Cement that solicited suggestions for the chemical composition of two new SRMs. A copy of the letter is reproduced in Appendix D. The majority of nearly 50 responses expressed the following desires:

1. SO_3 content should be greater than 2.50%, preferably near 3.00% or 3.50%.
2. K_2O content should be between 0.6% and 1.0%.
3. Na_2O content should be between 0.2% and 0.6%.
4. MgO content should be approximately 2.5% or 5.0%.
5. Fe_2O_3 content should be approximately 3.25% or 5.0%.
6. Al_2O_3 content should be approximately 4.8% or 5.2%.
7. SiO_2 content should be approximately 20% or 22%.
8. CaO content should be approximately 63% or greater than 66%.

A few respondents requested a low-iron, high-alumina cement, while a few other respondents wanted higher levels of trace elements (such as Cr, Zn, and Mn) than appeared in the "600 series" SRM. Several respondents suggested use of cements with which they were familiar, none of which appeared to satisfy the majority's requests. Therefore, it was decided to locate two or more cements that either alone or blended together would meet the needs of the majority of surveyed respondents.

After evaluating typical analyses from more than a dozen commercially available cements, approximately 200 kg of Type I portland cement was obtained from the St. Marys Cement Company in St Marys, Ontario, and the Texas Cement Company in Buda, Texas to be issued as SRM 1880. XRF analyses of each cement indicated that a 50:50 blend would produce a standard with levels of most elements very close to the desired concentration (see Appendix F).

To eliminate segregation of the packaged SRM, the cements were ground and classified separately in a Vortec M-1 impact mill and Vortec C-13 air classifier until all of the cement particles were between 0.5 and 45 μm as measured by a Micromeritics Sedi Graph* particle size analyzer (see Appendix F).

Approximately 100 kg of each cement was weighed and transferred to a 19-ft. steel ribbon blender and mixed for 2-1/2 hours. One-third of the cement was transferred to a plastic-lined 55-gal steel drum; the next third was caught in a plastic-lined 30-gal steel drum; and the final third was transferred to the same 55-gal drum. The cement in the smaller drum was then tested for

* In order to adequately describe materials and experimental procedures, it was occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Bureau of Standards nor does it imply that the particular products or equipment is necessarily the best available for the purpose.

homogeneity by analyzing 18 grab samples for sulfur, iron, and loss-on-ignition in accordance with ASTM C114 refer procedures (see Table 22). To improve the homogeneity, the cement was returned to the blender and mixed for four additional hours and then transferred as before. Six grab samples from the 30-gal drum were analyzed for iron with the results indicated in Table 22. These results verified that the cement was well blended and ready for packaging.

Table 22. Homogeneity of Blended Cements, SRM 1880, % by wt.

	2-1/2 Hours			6-1/2 Hours
Blender	SO_3	Fe_2O_3	Ign. Loss	Fe_2O_3
Top	3.69±0.014	2.93±0.000	1.40±0.010	2.81±0.000
Middle	3.68±0.021	2.91±0.028	1.36±0.005	2.82±0.021
Bottom	3.68±0.000	2.94±0.057	1.38±0.017	2.81±0.014

The approximate composition of the second cement standard was selected after considering the survey responses and the final composition of SRM 1880. In consultation with cement industry representatives, it was decided that SRM 1881 should have greater than 1% K_2O, greater than 4.5% Fe_2O_3, and a SO_3 level near 3.75%. After evaluating typical analyses from many commercially available cements, it was decided that a research cement identified as LTS-41 came closest to the desired composition. This cement had been obtained in 1941 and stored in steel drums in PCA since that time. It was manufactured by the former Alpha Portland Cement Company in Birmingham, Alabama. By testing the cement for loss-on-ignition, it was concluded that the cement had not gained significant moisture during storage.

To discourage segregation of the packaged SRM, the cement was ground and classified in a Vortec M-1 impact mill and Vortec C-13 air classifier until the cement particles were less than 40 μm (see Appendix F). Approximately 72 kg of cement was processed in this manner.

Because additional gypsum was needed to increase the SO_3 content to the desired level of 3.75%, several methods of blending (homogenizing) the cement with gypsum were studied, including paddle mixing and ball milling. A 0.14-m mortar mixer with rubber wiper blades was tried first with 91 kg of a test cement and 1.6 kg of gypsum. After mixing for 60 minutes there seemed to be a difference between samples taken from the top and bottom of the mixer. These samples were tested for total sulfur using a Leco sulfur analyzer. A 0.07-m ceramic-lined mill was tried next with equal charges (22 kg) of cement and gypsum and alumina balls (equal weights of 1-in, 3/4-in, and 1/2-in diameters). After milling for 60 minutes the blending was questionable. A 0.14-m steel-lined ball mill was tried next using the same ratio of balls to the cement charge. The results obtained in this test were more encouraging. Based on these results and discussions with members of the PCA staff, it was decided to use a ratio of 3 to 1 of high-density (90%) alumina balls to the cement and gypsum charge in the steel-lined mill.

To simulate the particle size distribution of gypsum typically found in cements, the gypsum was first ground to high fineness in a small (0.03 m) steel ball mill with 34 kg steel balls graded from 1/2 in to 7/8 in. Approximately 4 kg gypsum was added and ground at 70 rpm for 7500 revolutions. The mill was

stopped every 1500 revolutions and the gypsum scraped from the inner mill wall. The gypsum was discharged through a grate by turning the mill an additional 200 revolutions. This finely ground gypsum contained 2.1% greater than 200 mesh (70 μm). The entire batch was brushed through a 200 mesh sieve yielding about 3.9 kg with a Blaine specific surface area of 10,725 cm^3/g (density = 2.37 g/cm^3, bed porosity = 0.50).

The ground and classified cement was split into three batches of 24 kg each, homogenized separately for 10 minutes and then discharged into separate containers. Chemical analysis on composite grab samples indicated 1.67% SO_3 in the cement. To achieve the desired level of SO_3, approximately 1.2 kg of Terra Alba gypsum was added to each batch.

Each 24-kg batch of the cement was then blended separately in the steel-lined ball mill with 66-kg alumina balls graded as previously described. The mill was turned at 30 rpm for 15 minutes, stopped, the inner wall scraped, and the mill turned for an additional 15 minutes. The mill was then stopped, a discharge grate attached, and the mill turned for 5 minutes to discharge the cement. This blended cement was returned to its original container. Each of the three batches was homogenized in this manner and cross-blends between the batches were made according to the scheme shown in Figure 8. Grab samples taken from different locations in the mill during blending indicated satisfactory homogenization was achieved.

After blending, 12 grab samples of about 10 g each were taken to check the homogeneity. Because the cement was in three 5-gal cans, two samples were taken from the upper and lower halves of each can. Briquets were pressed from 6 g of each sample for XRF analysis for calcium, sulfur, and iron. The results of these preliminary homogeneity analyses are shown in Table 23. These results verified that the cement was well blended and ready for packaging.

Table 23. Prepackaging Homogeneity of SRM 1881, % by wt.

	CaO			SO_3			Fe_2O_3		
Can	1	2	3	1	2	3	1	2	3
Top	60.00	60.02	59.95	3.90	3.88	3.90	5.00	4.98	4.97
Bot.	60.03	59.88	60.19	3.90	3.92	3.94	5.00	4.99	5.00

SRMs 1880 and 1881 were packaged in one-dram stoppered shell vials, flame sealed within slightly larger shell vials, using the same method as the previous cement standards. A small glass wool disc placed in the outer vial protected the bottom of the inner vial during the flame sealing. See Appendix E for complete descriptions of the packaging materials.

During the first phase of preparing these two SRMs, PCA investigated the possibility of packaging the cements in modern flexible materials. See Appendix G for details on this study.

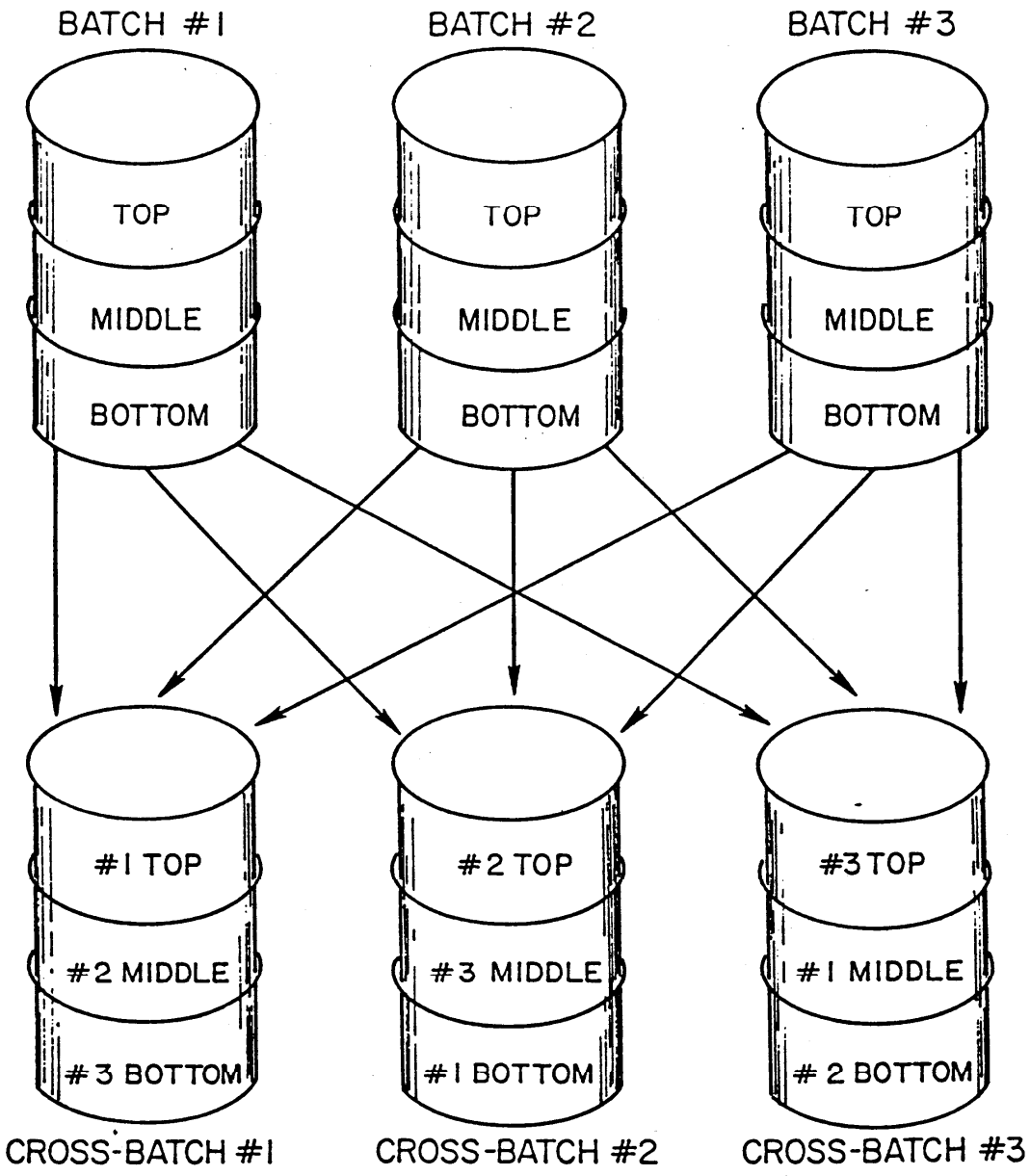

Figure 8. Scheme for mixing and blending the cement for SRM 1881

An auger-type apparatus was used to fill each vial with cement. A 4-gal hopper was manually loaded with cement and the vials were then filled by pressing a foot pedal to discharge the cement into one vial at a time. Approximately 20 vials per minute could be filled, each with 5 g of cement. The mass of cement going into each vial was checked with an electronic analytical balance several times each day. The vial was then stoppered and placed upside-down into a larger outer vial. The glass-wool pad was pushed down into the outer vial so that it rested against the bottom of the inner vial. The vials were then placed on a conveyor to the flame sealing machine. The sealing machine could seal about 18 vials per minute. The controls for flame size and temperature and vial rotation speed were all adjusted to produce uniform, hemispherical glass seals.

As the vials were conveyed away from the sealing machine, they were placed by hand into cardboard trays. Usually, one operator performed this work for 30 minutes and then exchanged places with the person operating the filling machine. Two additional people worked to cap and insert the vials. Three people could fill and seal about 3,000 vials per day. An entire lot of 10,000 vials was packaged in three and one-half days.

The methods used in the chemical analysis of SRMs 1880 and 1881 were the same as those used for the "600 series" SRMs, including the checking of precipitates and filtrates for impurities. A 0.5-g sample was used in all cases. For the majority of the analyses, tests were performed on some of ten samples chosen by stratified random selection such that each sample represented a single case of the stored cement. Ten of the 12 cases were picked at random. The ten samples permitted the chemists to perform analyses in sets of six (five unknowns and one blank or standard sample).

Silica

SiO_2 was determined by the classical double dehydration technique. The results of these determinations, as well as the confirming AAS results, are indicated in Table 24.

Table 24. Results of the Analyses of SiO_2, % by wt.

	Gravimetric			AAS		
SRM	Average	n	Std Dev	Average	n	Std Dev
1880	19.82	7	0.053	19.68	5	0.079
1881	22.25	4	0.029	22.22	5	0.069

"R_2O_3" Group (Al_2O_3, Fe_2O_3, P_2O_5, TiO_2, Cr_2O_3, and ZnO)

The combined group "R_2O_3" was determined by the classical double precipitation method. See Tables 25 through 29 for the results.

Table 25. Results of the Analyses of the "R_2O_3" Group, % by wt.

SRM	Average	n	Std Dev
1880	8.47	7	0.066
1881	9.19	4	0.026

Iron Oxide

Fe_2O_3 was determined on separate samples by the volumetric titration method and confirmed by AAS. See Table 26.

Table 26. Results of the Analyses of Fe_2O_3, % by wt.

	Volumetric			AAS		
SRM	Average	n	Std Dev	Average	n	Std Dev
1880	2.91	3	0.006	2.88	5	0.010
1881	4.68	4	0.005	4.71	5	0.030

Titania

TiO_2 in SRM 1880 was determined by a colorimetric method using Tiron reagent. In SRM 1881 it was also determined by XRF using standard additions. The ASTM C114 colorimetric method (complexation with Tiron) produces slightly low values. This procedure requires a correction due to interference by iron in the sample. Extensive investigations of this method during the analysis of these SRMs revealed the precise amount of correction to be applied. It also revealed the existence of some unknown interference which produces low values for TiO_2 in cements. In checking the notes made during the original definitive analyses of the "600 series" cements, it was found that all values obtained by the Tiron method had been adjusted to agree with check samples from "1000 series" cements, which had been analyzed for TiO_2 by the classical peroxide method.

To determine accurate values for TiO_2 in these SRMs, analyses were performed by the method of standard additions using both XRF and colorimetry. Samples were fused with NaOH for colorimetry or with $Li_2B_4O_7$ for XRF. Standard additions of TiO_2 (using SRM 154b) were made in increments of 0.25% up to a total of 1.25% TiO_2 for both methods. The net optical absorbances and net XRF intensities were plotted linearly against concentration. The concentrations of TiO_2 in the samples were determined by extrapolation to zero measurement response. The results are given in Table 27. Additional tests of the "600 series" cements indicated that the present values are correct.

Table 27. Results of the Analyses of TiO_2, % by wt.

	Colorimetric			XRF
SRM	Average	n	Std Dev	
1880	0.230	10	0.003	
1881	0.248	2	0.002	0.217

Phosphorus Oxide

P_2O_5 was determined on separate samples by the "molybdenum blue" colorimetric method. See Table 28 for the results.

Table 28. Results of the P_2O_5, % by wt.

SRM	Average	n	Std Dev
1880	0.292	10	0.001
1881	0.091	4	0.001

Zinc Oxide

ZnO was determined on separate samples by AAS using a standard addition technique. The value for each SRM was found to be 0.01 percent.

Chromium Oxide

Cr_2O_3 was determined on a separate sample by AAS. The value for each SRM was found to be less than 0.01 percent.

Alumina

Al_2O_3 was determined by difference (subtracting the amounts of Fe_2O_3, TiO_2, P_2O_5, and ZnO from the "R_2O_3" group amount) and confirmed by AAS. See Table 29 for the results.

Table 29. Results of the Analyses of Al_2O_3, % by wt.

	By Difference				AAS		
SRM	"R_2O_3"	"X_2O_3"	Al_2O_3	Std Dev	Average	n	Std Dev
1880	8.47	3.44	5.03	0.064	5.05	4	0.037
1881	9.19	5.03	4.16	0.030	4.21	5	0.034

Manganese Oxide

Mn_2O_3 was determined on separate samples by AAS. See Table 30 for the results.

Table 30. Results of the Analyses of Mn_2O_3, % by wt.

SRM	Average	n	Std Dev
1880	0.08	5	0.000
1881	0.26	5	0.000

Calcium Group

CaO + SrO was determined by the classical double precipitation method using ammonium oxalate. See Table 31 for the results.

Table 31. Results of Analyses of the Calcium Group, % by wt.

SRM	Average	n	Std Dev
1880	63.09	6	0.064
1881	58.65	4	0.054

Strontium Oxide

The value of SrO for certification was determined on separate samples by AAS. The amount of SrO in the Calcium oxide precipitate was also determined by AAS. These values are given in Table 23.

Table 32. Results of the Analyses of SrO, % by wt.

	Separate Samples			CaO Precipitate		
SRM	Average	n	Std Dev	Average	n	Std Dev
1880	0.06	5	0.005	0.04	7	0.004
1881	0.11	5	0.000	0.09	3	0.002

Magnesia

MgO was determined by the classical double precipitation method. This value is corrected for the small amount of CaO in the precipitate as determined by AAS. This corrected value is confirmed by measurements on separate samples by AAS. See Table 33 for the results.

Table 33. Results of the Analyses of MgO, % by wt.

	Gravimetric			CaO in		AAS		
SRM	Average	n	Std Dev	MgO*	Difference	Average	n	Std Dev
1880	2.75	7	0.032	0.06	2.69	2.65	5	0.014
1881	2.70	4	0.009	0.07	2.63	2.65	5	0.008

*See correction factor on page 20.

Calcium Oxide

CaO was determined by difference (subtracting the amount of strontium in the group precipitate and adding the amount of calcium in the magnesium precipitate). See Table 34 for the results.

Table 34. Results of the Analyses of CaO, % by wt.

SRM	SrO + CaO	SrO in CaO	CaO in MgO	CaO	Std Dev
1880	63.09	0.04	0.09	63.14	0.07
1881	58.65	0.09	0.11	58.67	0.06

Sulfur Oxide

SO_3 was determined on separate samples using a precipitation with barium chloride. The amount of SO_3 in a composite sample of SRM 1881 was also determined by ion chromatography calibrated against standard sulfate solutions. These results are indicated in Table 35.

Table 35. Results of the Analyses of SO_3, % by wt.

	Gravimetry			Chromatography
SRM	Average	n	Std Dev	
1880	3.37	5	0.013	
1881	3.65	5	0.021	3.69

Potassium and Sodium Oxides

These alkalies were determined on separate samples by AAS. See Tables 36 and 37 for the results.

Table 36. Results of the Analyses of K_2O, % by wt.

SRM	Average	n	Std Dev
1880	0.91	5	0.007
1881	1.17	5	0.009

Table 37. Results of the Analyses of Na_2O, % by wt.

SRM	Average	n	Std Dev
1880	0.28	5	0.000
1881	0.04	5	0.000

Fluoride

Fluoride was determined on separate samples by a specific ion electrode procedure. The results are indicated in Table 38.

Table 38. Results of the Analyses of Fluoride, % by wt.

SRM	Average	n	Std Dev
1880	0.104	10	0.0008
1881	0.094	5	0.0004

Chloride

Chloride was determined on separate samples by a potentiometric titration procedure [6]. In this procedure the sample is decomposed in nitric acid, filtered, and titrated potentiometrically with silver nitrate using a Ag/AgS electrode. See Table 39 for the results.

Table 39. Results of the Analysis of Chloride, % by wt.

SRM	Average	n	Std Dev
1880	0.016	9	0.0015
1881	0.005	5	0.0005

Miscellaneous Elements

No significant amounts (less than 0.01 percent) of barium, boron, and zirconium were found.

Ignition Loss

Loss-on-ignition (1000 °C for 30 minutes) was determined on separate samples. See Table 40.

Table 40. Results of Ignition Loss, % by wt.

SRM	Average	n	Std Dev
1880	1.38	4	0.019
1881	2.01	5	0.018

The combined results of all these analyses are given in Table 41 along with the pooled standard deviations for the two cements. These results formed the basis for the certification of SRMs 1880 and 1881.

Table 41. Final Results for SRMs 1880 and 1881, % by wt.

	SRM		
Constituent	1880	1881	S_p
CaO	63.14	58.67	0.06
SiO_2	19.82	22.25	0.05
Al_2O_3	5.03	4.06	0.06
Fe_2O_3	2.91	4.68	0.01
SO_3	3.37	3.65	0.02
MgO	2.69	2.63	0.03
K_2O	0.91	1.17	0.01
TiO_2	0.23	0.25	<0.01
Na_2O	0.28	0.04	<0.01
SrO	0.06	0.11	<0.01
P_2O_5	0.29	0.09	<0.01
Mn_2O_3	0.08	0.26	<0.01
F	0.10	0.09	<0.01
Cl	0.02	0.01	<0.01
ZnO	0.01	0.01	
Cr_2O_3	<0.01	<0.01	
Ign Loss	1.38	2.01	0.02
Total	100.2	100.0	

S_p is the pooled standard deviation for the two SRMs.

Conclusion

During the preparation of SRMs 1880 and 1881, several methods of blending (homogenizing) the cements were studied. The effectiveness of a ribbon-type blender, a paddle mixer, a rotating drum mixer, a ceramic pebble, and steel ball mills were tested. The paddle and drum mixers performed poorly, actually causing a segregation in the samples. The pebble mill performed well with a ball-charge to sample weight ration of 3:1. However, extended time in the ball mill produced a sample of greater fineness. Thus, of the blenders tested, the ribbon blender worked best, yielding flowable powders; unfortunately, it is tedious to thoroughly clean because of the arrangement of the ribbon blades. A systematic study should be made to determine the effectiveness of twin-shell "V-blenders" with high-speed intensifier bars.

The traditional flame sealed glass vials are excellent containers for portland cement SRMs. Samples of cement which were sealed in glass vials and stored in a 100%-relative-humidity room for two years showed no increase in loss-on-ignition or change in specific area. A sample of SRM 114, Portland Cement Fineness Standard, which had been sealed in glass vials for more than three decades is still being used. The filling and sealing of glass vials, however, is a slow process. On the other hand, flexible packages offer the advantages of light weight, a large surface for labelling, high-speed filling and sealing with automated apparatus, and they will not break if dropped. The use of flexible packages, however, are doubtful. See Appendix G for a study of their performance under extreme conditions. While they can provide good barriers against moisture and carbon dioxide, they are not intended for long-term storage of materials, because the plastic films may deteriorate. Therefore, developments in the flexible packaging industry should be monitored. When plastic laminates become available with extended life, they should be carefully tested for their suitability as containers. It is noted that the Cement Association of Japan has begun to use flexible packages for their portland cement fineness standards.

Since the completion of SRMs 1880 and 1881, a computer program was written by R. Paule, P. Pella, and G. Y. Tao of NBS which performs a rigorous within and between analysis of variance. This program eliminates the use of "judgement" when assessing the variability of homogenized samples. It is based on performing duplicate XRF analyses of samples fused with lithium tetraborate. The program should be employed in evaluating the blending of cement SRMs in the future.

Significant interferences found during the course of the analytical studies are:

(1) Approximately 0.1% CaO is found in the MgO precipitate. This correction should be made for accurate MgO determinations.

(2) The gravimetric procedure for CaO has been replaced in ASTM C114-83a with a titration procedure. Because the gravimetric procedure is subject to interferences from strontium and magnesium, future analyses for certification of calcium in cements should be based on the titration and other instrumental methods.

(3) The gravimetric aluminum determination is also subject to interferences, notably through the presence of phosphorus, titanium, and iron. If present in sufficient quantities, chromium, zinc, and copper also interfere. Thus, future analyses for aluminum in cements should be based on instrumental methods.

(4) The colorimetric method for titanium (using Tiron reagent) described in ASTM C114 and studied during the characterization of SRM 1881 gives values that are consistently several hundredths of a percent low. The influence of iron on the determination was investigated and its influence is now known. It does not, however, account for the remaining consistently low values. Further work is needed on this method.

The analytical program has demonstrated that several interferences exist that must be taken into account to obtain the most accurate values when performing gravimetric determinations. On the other hand, instrumental analysis has reached a high level of reliability, precision and accuracy so that many analyses previously performed by classical methods can be replaced by techniques such as atomic absorption/emission, x-ray fluorescence, neutron activation, mass spectroscopy, and plasma emission.

Perhaps the most significant difficulty in performing classical gravimetric analyses is simply that fewer and fewer chemists practice these methods and the precision and accuracy of these techniques depend on the skill of the analyst. It is a tribute to the analysts who participated in this program, notably Robert F. Crow of the PCA laboratories, that the gravimetric results are in excellent agreement with those of the instrumental techniques.

Acknowledgements

The preparation, packaging, and characterization of these portland cement SRMs was accomplished through the close cooperation of many people and organizations. Special credits are given to those listed below.

NBS Staff
Leonard Bean
Bruce E. Foster
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Celestino Palmiano
Heinz Seiler
Charles Wilk

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ASTM Committee C-1 on Cement
The many cement manufacturers who contributed the cements from which the SRMs were made and for extensive laboratory time in performing analyses.

References

[1] ASTM C114-69, Standard Methods for Chemical Analysis of Hydraulic Cement, American Society for Testing and Materials, Annual Book of ASTM Standards, Part 9.

[2] Jugovic, Z. T., Application of Spectrophotometric and EDTA Methods for Rapid Analysis of Cement and Raw Materials, in Analytical Techniques for Hydraulic Cement and Concrete, ASTM Standard Technical Publication, STP No. 395, 1966, pp. 65-93.

[3] Crow, R. F. and Connolly, J. D., Atomic Absorption Analyses of Portland Cement and Raw Mix Using a Lithium Metaborate Fusion, Journal of Testing and Evaluation (ASTM), Vol. 1 (No. 5), September 1973, pp. 382-393.

[4] Crow, R. F. and Connolly, J. D., Analysis of Portland Cement, Prog. Analyt. Atom. Spectrosc., Vol. 1, 1979, p. 349.

[5] Peck, L. C., Systematic Analysis of Silicate, U. S. Geological Survey Bulletin 1170, 1964.

[6] Mivelaz, W. F. et al., Test Methods of the PCA Analytical Chemistry Laboratories, Portland Cement Association, February 1980, Sec. 4, pp. 1-20.

Copies of the reports

(1) Cooperative Analyses of the "600 series" SRMs.

(2) Definitive Analysis of the "600 series" SRMs.

(3) Preparation and Analysis of SRM 1880.

(4) Preparation and Analysis of SRM 1881.

can be obtained from the Office of Standard Reference Materials, National Bureau of Standards.

Appendix A

Copies of the certificates:

SRM 177
1011
1013
1014
1015
1016
633
634
635
636
637
638
639
1880
1881

UNITED STATES DEPARTMENT OF COMMERCE
WASHINGTON 25, D. C.

National Bureau of Standards

Certificate of Analyses

Standard Sample 177
Portland Cement

ANALYST	SiO_2	Al_2O_3	Fe_2O_3	[a] TiO_2	P_2O_5	[b] CaO	SrO	MgO	SO_3	Mn_3O_4	Na_2O	K_2O	[c] Loss on Ignition
1	21.91	5.26	[d] 2.43, 2.40	0.26	[e] 0.05	64.29	[f] 0.05	2.43	1.59	[g] 0.05	[h] 0.15, [i] .15	[h] 0.57, [i] .55	1.11
2	21.88	5.28	[j] 2.39	.28	[k] .05	64.28	[f] .05	2.42	1.59	.05	[l] .14	[l] .57	1.11
3	[m] 21.96	5.20	2.38	.28	[k] .04, [n] .04	64.41		2.46	1.56	.04	[l] .14	[l] .57	1.15
4	21.90	[o] 5.38	2.40	.25		64.27		2.45	1.63	[g] .04	[p] .15	[p] .59	1.19
5	21.96	[o] 5.50	2.38		.03	64.37		2.48	1.56	.04			1.19
6	[l] 21.91	[l] 5.26	[l] 2.37	.28		[l] 64.26		[l] 2.51	[l] 1.55	[g] .05	[p] .13	[p] .56	[l] 1.04
7	21.93	5.25	2.39	.24	.04	64.37		2.50	1.60	.06	[p] .12	[p] .56	1.17
8	21.85	5.26	2.39	.22	.04	64.40		2.37	1.55	.03	[i] .12	[i] .60	1.17
9	[q] 21.97	5.24	2.36	.27	[k] .05, [n] .05	[r] 64.56		2.48	1.62	[g] .04	[p] .13	[p] .56	1.16
10	21.90	[l,o] 5.76	[l] 2.45		.05	[l] 64.35		[l] 2.48	[l] 1.60	.06	[l] .13	[l] .58	[l] 1.14
11	21.93	5.36	2.36	.24	.03	64.27		2.40	1.58	.04	[i] .12, [p] .12	[i] .51, [p] .55	1.18
12	21.94	5.31	2.38	.26	.04	64.18		2.48	1.61	.04	[i] .16, [r,p] .11	[p] .57	1.14
13	[m] 21.87	5.30	2.37	.25	.05	64.38		[r] 2.44	1.60	.06	[p] .13	[p] .58	1.15
Average	21.92	5.27	2.39	0.26	0.04	64.32	0.05	2.45	1.59	0.05	0.14	0.57	1.15

[a] H_2O_2-photometric method (ASTM Spec. C114-56T).
[b] All values for CaO include SrO.
[c] 1 g heated at 900° to 1,000° C. for 15 min. in a covered platinum crucible (ASTM Spec. C114-53).
[d] NH_4CNS-photometric.
[e] Molybdenum-blue photometric.
[f] Flame photometric. See Anal. Chem. 27, 913 (1955).
[g] Periodate photometric.
[h] Flame photometric. Silica removed by HF-$HClO_4$ treatment.
[i] Gravimetric. Decomposition with NH_4Cl-$CaCO_3$. (ASTM Spec. C114-53.)
[j] Includes 0.12 FeO converted to Fe_2O_3.
[k] Phosphovanadomolybdate method.
[l] Federal Test Methods, Standard No. 158 (1957).
[m] NH_4Cl-HCl digestion. ASTM alternate method (C114-53).
[n] Gravimetric, weighed as $Mg_2P_2O_7$.
[o] Omitted from average, value includes TiO_2 or P_2O_5.
[p] Flame photometric (ASTM Spec. C114-56T).
[q] Double dehydration with $HClO_4$ with intervening filtration.
[r] Not included in the average.
Analyst 1 reported 0.004-percent Li_2O.

List of Analysts

1. Keith M. Sappenfield and R. A. Paulson, Analytical Chemistry Section, National Bureau of Standards.
2. Joseph R. Spann and J. J. Diamond, Concreting Materials Section, National Bureau of Standards.
3. Harold Allen, Nonbituminous Section, Bureau of Public Roads, Washington, D. C.
4. F. S. Reagel and O. E. Brown, Marquette Cement Manufacturing Co., Chicago, Ill.
5. W. J. Limbach, Southwestern Portland Cement Co., Fairborn, Ohio.
6. Walter H. Price, Division of Engineering Laboratories, Bureau of Reclamation, Denver, Colo.
7. F. P. Diener and O. A. Ellingson, Universal Atlas Cement Co., New York, N. Y.
8. L. R. Indermuehle, Southwestern Portland Cement Co., Victorville, Calif.
9. K. E. Palmer, Ideal Cement Co., Fort Collins, Colo.
10. L. R. Pritchard, Lone Star Cement Corporation, New York, N. Y.
11. W. C. Hanna and Leon Loomis, California Portland Cement Co., Colton, Calif.
12. W. J. McCoy and O. L. Eshenour, Lehigh Portland Cement Co., Research Laboratory, Coplay, Pa.
13. J. H. Walker, Portland Cement Association, Chicago, Ill.

WASHINGTON, D. C., November 25, 1957.

A. V. ASTIN, *Director.*

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C. 20234

PROVISIONAL CERTIFICATE OF ANALYSIS
STANDARD SAMPLE 1011
PORTLAND CEMENT

	Percent
SiO_2	21.03
Al_2O_3	5.38
Fe_2O_3	2.07
TiO_2	0.25
P_2O_5	.33
CaO (+SrO)	66.60
SrO	0.11
MgO	1.12
SO_3	1.75
Mn_2O_3	0.03
Na_2O	.08
K_2O	.26
Li_2O	(.002)
Rb_2O	(.001)
Loss on Ignition	1.13

Values in parentheses are not certified but are given as added information.

A. A. Bates, Chief
Building Research Division

Washington, D. C.
Revised Certificate, April 24, 1964
Original Certificate January 17, 1962

USCOMM-NBS-DC

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
L. M. Branscomb, Director

Certificate of Analysis

STANDARD REFERENCE MATERIAL 1013

Portland Cement

	Percent
SiO_2	24.1_7
Al_2O_3	3.30
Fe_2O_3	3.07
TiO_2	0.20
P_2O_5	.20
CaO (+ SrO)	64.3_4
SrO	0.08
MgO	1.39
SO_3	1.80
Mn_2O_3	0.05
Na_2O	.20
K_2O	.32
Li_2O	(.001)
Rb_2O	(.004)
Loss on Ignition	.99

PROVISIONAL

Values in parentheses are not certified but are given as added information.

Washington, D. C. 20234
January 17, 1962
(Revised April 24, 1964)
(Reprinted March 16, 1970)

A. A. Bates, Chief
Building Research Division

U. S. Department of Commerce
Maurice H. Stans
Secretary

National Bureau of Standards
. M. Branscomb, Director

Certificate of Analysis

Standard Reference Material 1014

Portland Cement

	Percent
SiO_2	19.4$_9$
Al_2O_3	6.38
Fe_2O_3	2.50
TiO_2	0.25
P_2O_5	.32
CaO (+SrO)	63.3$_6$
SrO	0.26
MgO	2.80
SO_3	2.70
Mn_2O_3	0.07
Na_2O	.24
K_2O	.99
Li_2O	(.005)
Rb_2O	(.007)
Loss on Ignition	.81

PROVISIONAL

Values in parentheses are not certified but are given as added information.

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(Reprinted June 18, 1971)

A. A. Bates, Chief
Building Research Division

U. S. DEAPRTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D.C. 20234

PROVISIONAL CERTIFICATE OF ANALYSIS
STANDARD SAMPLE 1015
PORTLAND CEMENT

	Percent
SiO_2	20.65
Al_2O_3	5.04
Fe_2O_3	3.27
TiO_2	0.26
P_2O_5	.05
CaO (+ SrO)	61.48
SrO	0.11
MgO	4.25
SO_3	2.28
Mn_2O_3	0.06
Na_2O	.16
K_2O	.87
Li_2O	(.004)
Rb_2O	(.005)
Loss on Ignition	1.70

Values in parentheses are not certified but are given as added information.

A. A. Bates, Chief
Building Research Division

Washington, D. C.
Revised Certificate, April 24, 1964
Original Certificate January 17, 1962

USCOMM-NBS-DC

U. S. Department of Commerce
C. R. Smith
Secretary

National Bureau of Standards
A. V. Astin, Director

Certificate of Analysis

STANDARD SAMPLE 1016
PORTLAND CEMENT

	Percent
SiO_2	21.05
Al_2O_3	4.97
Fe_2O_3	3.71
TiO_2	0.34
P_2O_5	.13
CaO (+SrO)	65.26
SrO	0.25
MgO	.42
SO_3	2.27
Mn_2O_3	0.04
Na_2O	.55
K_2O	.04
Li_2O	(.012)
Rb_2O	*(N.D.)
Loss on Ignition	1.20

PROVISIONAL

Values in parentheses are not certified but are given as added information.
*N.D. = not detected, but less than 0.001%

A. A. Bates, Chief
Building Research Division

Washington, D. C.
Revised Certificate April 24, 1964
Original Certificate January 17, 1962
Certificate Reprinted January 17, 1969

USCOMM-NBS-DC

U.S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 633

Portland Cement
(Cap Color is Red)

This Standard Reference Material (SRM) is intended for use in checking chemical methods of analysis and in calibration of instrumental methods of analysis.

The value listed for a constituent is the *present best estimate* of the "true" value based on the results of a definitive analysis program carried out in the laboratories of the Portland Cement Association by N. R. Greening, W. F. Mivelaz and R. F. Crow, with W. G. Hime of Erlin, Hime Associates acting as consultant. The certified value for a constituent is not expected to deviate from the "true" value by more than ±1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ±5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than those uncertainty figures.

Constituent	Percent by Weight	Constituent	Percent by Weight
CaO[a]	64.5_0	Na_2O	0.64
SiO_2	21.8_8	SrO	.31
Al_2O_3	3.7_8	P_2O_5	.24
Fe_2O_3	4.20	Mn_2O_3	.04
SO_3	2.2_0	F	.08
MgO[a]	1.0_4	ZnO	.01
K_2O	0.17	Cr_2O_3	.01
TiO_2	.24	Ign. loss	$.7_5$
		Total[b]	100.06

[a]If the procedures of ASTM C114 are followed a small amount of CaO will remain in the MgO precipitate. In this case the uncorrected values given below for CaO and MgO should be used.

CaO	64.4_7
MgO	1.0_6

[b]A correction has been made for the amount of fluoride present. This correction, which was subtracted from the gross total, was determined by multiplying the percent fluoride by the ratio of the atomic weight of oxygen to the molecular weight of fluorine (0.421).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by B. E. Foster, R. E. Michaelis, and C. L. Stanley.

Washington, D.C. 20234
December 15, 1983
(Revision of certificates
dated 2-24-77 and 6-12-74)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(Over)

HOMOGENEITY TESTING: Measurements were made at NBS on the portland cement supplied by the Lone Star Cement Corporation by S. D. Rasberry, M. M. Darr, and J. McKay by x-ray fluorescence analysis. The cement was sampled at 16 locations and two briquettes were prepared for each one. Calcium and sulfur, chosen as key elements for checking inhomogeneity, were determined by making four independent measurements on each briquette. A trend-elimination statistical design was employed in measuring the specimens. An analysis of these data indicated the homogeneity was satisfactory. Following these measurements the cement was thoroughly blended and packaged in hermetically sealed glass vials by personnel of the Cement and Concrete Research Laboratory and the Office of Standard Reference Materials.

DEFINITIVE ANALYSIS PROGRAM OF THE PORTLAND CEMENT CORPORATION: "Wet" chemical gravimetric methods were used for the major constituents CaO, SiO_2, Al_2O_3 and MgO. (The methods were essentially those of ASTM C114 using a 0.5-g sample.) Fe_2O_3 was determined by dichromate titration and SO_3 by precipitation in an acid solution after removal of the ammonium hydroxide group and silica. Atomic absorption spectroscopy techniques were used for K_2O, Na_2O, SrO, Mn_2O_3, ZnO and Cr_2O_3. Colorimetric techniques were used to determine TiO_2 and P_2O_5 while fluoride was determined by an ion selective electrode method. Loss on ignition was determined at 1000°C. In each determination duplicate measurements were made on two to ten randomly selected samples. Through the use of various techniques (colorimetric, gravimetric, potentiometric, optical emission elements were determined to be less than 0.01 wt%: Cl, Ba, Zr, B, V, Ni, Mo, Sn, Pb, Cu, and Ag. The total of 100.06% of the certified constituents in the cement corroborates the evaluation and indicates that significant biases have not been introduced.

CAUTION: To obtain the most accurate results by x-ray fluorescent methods of analysis, the user should compare his samples to the particular SRM that is most nearly the same in overall chemical composition. Alternatively, inter-element effect calibration procedures may be adopted to minimize biases.

U.S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 634

Portland Cement
(Cap Color is Gold)

This Standard Reference Material (SRM) is intended for use in checking chemical methods of analysis and in calibration of instrumental methods of analysis.

The value listed for a constituent is the *present best estimate* of the "true" value based on the results of a definitive analysis program carried out in the laboratories of the Portland Cement Association by N. R. Greening, W. F. Mivelaz and R. F. Crow, with W. G. Hime of Erlin, Hime Associates acting as consultant. The certified value for a constituent is not expected to deviate from the "true" value by more than ±1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ±5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than those uncertainty figures.

Constituent	Percent by Weight	Constituent	Percent by Weight
CaO[a]	62.5_8	Na_2O	0.15
SiO_2	20.7_3	SrO	.12
Al_2O_3	5.2_1	P_2O_5	.10
Fe_2O_3	2.84	Mn_2O_3	.28
SO_3	2.2_1	F	.08
MgO[a]	3.3_0	ZnO	.02
K_2O	0.42	Cr_2O_3	.08
TiO_2	.29	Ign. loss	1.6_2
		Total[b]	100.00

[a]If the procedures of ASTM C114 are followed a small amount of CaO will remain in the MgO precipitate. In this case the uncorrected values given below for CaO and MgO should be used.

CaO	62.5_4
MgO	3.3_3

[b]A correction has been made for the amount of fluoride present. This correction, which was subtracted from the gross total, was determined by multiplying the percent fluoride by the ratio of the atomic weight of oxygen to the molecular weight of fluorine (0.421).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by B. E. Foster, R. E. Michaelis, and C. L. Stanley.

Washington, D.C. 20234
December 15, 1983
(Revision of certificates
dated 2-24-77 and 6-12-74)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(Over)

HOMOGENEITY TESTING: Measurements were made at NBS on the portland cement supplied by the Universal Atlas Cement Division of United States Steel Corporation by S. D. Rasberry, M. M. Darr, and J. McKay by x-ray fluorescence analysis. The cement was sampled at 16 locations and two briquettes were prepared for each one. Calcium and sulfur, chosen as key elements for checking inhomogeneity, were determined by making four independent measurements on each briquette. A trend-elimination statistical design was employed in measuring the specimens. An analysis of these data indicated the homogeneity was satisfactory. Following these measurements the cement was thoroughly blended and packaged in hermetically sealed glass vials by personnel of the Cement and Concrete Research Laboratory and the Office of Standard Reference Materials.

DEFINITIVE ANALYSIS PROGRAM OF THE PORTLAND CEMENT CORPORATION: "Wet" chemical gravimetric methods were used for the major constituents CaO, SiO_2, Al_2O_3 and MgO. (The methods were essentially those of ASTM C114 using a 0.5-g sample.) Fe_2O_3 was determined by dichromate titration and SO_3 by precipitation in an acid solution after removal of the ammonium hydroxide group and silica. Atomic absorption spectroscopy techniques were used for K_2O, Na_2O, SrO, Mn_2O_3, ZnO and Cr_2O_3. Colorimetric techniques were used to determine TiO_2 and P_2O_5 while fluoride was determined by an ion selective electrode method. Loss on ignition was determined at 1000°C. In each determination duplicate measurements were made on two to ten randomly selected samples. Through the use of various techniques (colorimetric, gravimetric, potentiometric, optical emission elements were determined to be less than 0.01 wt%: Cl, Ba, Zr, B, V, Ni, Mo, Sn, Pb, Cu, and Ag. The total of 100.00% of the certified constituents in the cement corroborates the evaluation and indicates that significant biases have not been introduced.

CAUTION: To obtain the most accurate results by x-ray fluorescent methods of analysis, the user should compare his samples to the particular SRM that is most nearly the same in overall chemical composition. Alternatively, interelement effect calibration procedures may be adopted to minimize biases.

U.S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 635

Portland Cement
(Cap Color is Blue)

This Standard Reference Material (SRM) is intended for use in checking chemical methods of analysis and in calibration of instrumental methods of analysis.

The value listed for a constituent is the *present best estimate* of the "true" value based on the results of a definitive analysis program carried out in the laboratories of the Portland Cement Association by N. R. Greening, W. F. Mivelaz and R. F. Crow, with W. G. Hime of Erlin, Hime Associates acting as consultant. The certified value for a constituent is not expected to deviate from the "true" value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than those uncertainty figures.

Constituent	Percent by Weight	Constituent	Percent by Weight
CaO[a]	59.8_3	Na_2O	0.07
SiO_2	18.4_1	SrO	.21
Al_2O_3	6.2_9	P_2O_5	.17
Fe_2O_3	2.61	Mn_2O_3	.09
SO_3	7.0_7	F	.04
MgO[a]	1.2_3	ZnO	.01
K_2O	0.45	Cr_2O_3	.01
TiO_2	.32	Ign. loss	3.2_4
		Total[b]	100.03

[a]If the procedures of ASTM C114 are followed a small amount of CaO will remain in the MgO precipitate. In this case the uncorrected values given below for CaO and MgO should be used.

CaO	59.7_9
MgO	1.2_6

[b]A correction has been made for the amount of fluoride present. This correction, which was subtracted from the gross total, was determined by multiplying the percent fluoride by the ratio of the atomic weight of oxygen to the molecular weight of fluorine (0.421).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by B. E. Foster, R. E. Michaelis, and C. L. Stanley.

Washington, D.C. 20234
December 15, 1983
(Revision of certificates
dated 2-24-77 and 6-12-74)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(Over)

HOMOGENEITY TESTING: Measurements were made at NBS on the portland cement supplied by the Penn-Dixie Cement Corp. by S. D. Rasberry, M. M. Darr, and J. McKay by x-ray fluorescence analysis. The cement was sampled at 16 locations and two briquettes were prepared for each one. Calcium and sulfur, chosen as key elements for checking inhomogeneity, were determined by making four independent measurements on each briquette. A trend-elimination statistical design was employed in measuring the specimens. An analysis of these data indicated the homogeneity was satisfactory. Following these measurements the cement was thoroughly blended and packaged in hermetically sealed glass vials by personnel of the Cement and Concrete Research Laboratory and the Office of Standard Reference Materials.

DEFINITIVE ANALYSIS PROGRAM OF THE PORTLAND CEMENT CORPORATION: "Wet" chemical gravimetric methods were used for the major constituents CaO, SiO_2, Al_2O_3 and MgO. (The methods were essentially those of ASTM C114 using a 0.5-g sample.) Fe_2O_3 was determined by dichromate titration and SO_3 by precipitation in an acid solution after removal of the ammonium hydroxide group and silica. Atomic absorption spectroscopy techniques were used for K_2O, Na_2O, SrO, Mn_2O_3, ZnO and Cr_2O_3. Colorimetric techniques were used to determine TiO_2 and P_2O_5 while fluoride was determined by an ion selective electrode method. Loss on ignition was determined at 1000°C. In each determination duplicate measurements were made on two to ten randomly selected samples. Through the use of various techniques (colorimetric, gravimetric, potentiometric, optical emission elements were determined to be less than 0.01 wt%: Cl, Ba, Zr, B, V, Ni, Mo, Sn, Pb, Cu, and Ag. The total of 100.03% of the certified constituents in the cement corroborates the evaluation and indicates that significant biases have not been introduced.

CAUTION: To obtain the most accurate results by x-ray fluorescent methods of analysis, the user should compare his samples to the particular SRM that is most nearly the same in overall chemical composition. Alternatively, inter-element effect calibration procedures may be adopted to minimize biases.

U.S. Department of Commerce
Malcolm Baldrige
Secretary
National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 636

Portland Cement
(Cap Color is Yellow)

This Standard Reference Material (SRM) is intended for use in checking chemical methods of analysis and in calibration of instrumental methods of analysis.

The value listed for a constituent is the *present best estimate* of the "true" value based on the results of a definitive analysis program carried out in the laboratories of the Portland Cement Association by N. R. Greening, W. F. Mivelaz and R. F. Crow, with W. G. Hime of Erlin, Hime Associates acting as consultant. The certified value for a constituent is not expected to deviate from the "true" value by more than ±1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ±5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than those uncertainty figures.

Constituent	Percent by Weight	Constituent	Percent by Weight
CaO[a]	63.5_4	Na_2O	0.11
SiO_2	23.2_2	SrO	.04
Al_2O_3	3.0_2	P_2O_5	.08
Fe_2O_3	1.61	Mn_2O_3	.12
SO_3	2.3_1	F	.06
MgO[a]	3.9_5	ZnO	.03
K_2O	0.59	Cr_2O_3	.01
TiO_2	.18	Ign. loss	1.1_6
		Total[b]	100.00

[a]If the procedures of ASTM C114 are followed a small amount of CaO will remain in the MgO precipitate. In this case the uncorrected values given below for CaO and MgO should be used.

CaO	63.4_9
MgO	3.9_8

[b]A correction has been made for the amount of fluoride present. This correction, which was subtracted from the gross total, was determined by multiplying the percent fluoride by the ratio of the atomic weight of oxygen to the molecular weight of fluorine (0.421).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by B. E. Foster, R. E. Michaelis, and C. L. Stanley.

Washington, D.C. 20234
December 15, 1983
(Revision of certificates
dated 2-24-77 and 6-12-74)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(Over)

HOMOGENEITY TESTING: Measurements were made at NBS on the portland cement supplied by the Arizona Portland Cement Co. by S. D. Rasberry, M. M. Darr, and J. McKay by x-ray fluorescence analysis. The cement was sampled at 16 locations and two briquettes were prepared for each one. Calcium and sulfur, chosen as key elements for checking inhomogeneity, were determined by making four independent measurements on each briquette. A trend-elimination statistical design was employed in measuring the specimens. An analysis of these data indicated the homogeneity was satisfactory. Following these measurements the cement was thoroughly blended and packaged in hermetically sealed glass vials by personnel of the Cement and Concrete Research Laboratory and the Office of Standard Reference Materials.

DEFINITIVE ANALYSIS PROGRAM OF THE PORTLAND CEMENT CORPORATION: "Wet" chemical gravimetric methods were used for the major constituents CaO, SiO_2, Al_2O_3 and MgO. (The methods were essentially those of ASTM C114 using a 0.5-g sample.) Fe_2O_3 was determined by dichromate titration and SO_3 by precipitation in an acid solution after removal of the ammonium hydroxide group and silica. Atomic absorption spectroscopy techniques were used for K_2O, Na_2O, SrO, Mn_2O_3, ZnO and Cr_2O_3. Colorimetric techniques were used to determine TiO_2 and P_2O_5 while fluoride was determined by an ion selective electrode method. Loss on ignition was determined at 1000°C. In each determination duplicate measurements were made on two to ten randomly selected samples. Through the use of various techniques (colorimetric, gravimetric, potentiometric, optical emission elements were determined to be less than 0.01 wt%: Cl, Ba, Zr, B, V, Ni, Mo, Sn, Pb, Cu, and Ag. The total of 100.00% of the certified constituents in the cement corroborates the evaluation and indicates that significant biases have not been introduced.

CAUTION: To obtain the most accurate results by x-ray fluorescent methods of analysis, the user should compare his samples to the particular SRM that is most nearly the same in overall chemical composition. Alternatively, inter-element effect calibration procedures may be adopted to minimize biases.

U.S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 637

Portland Cement
(Cap Color is Pink)

This Standard Reference Material (SRM) is intended for use in checking chemical methods of analysis and in calibration of instrumental methods of analysis.

The value listed for a constituent is the *present best estimate* of the "true" value based on the results of a definitive analysis program carried out in the laboratories of the Portland Cement Association by N. R. Greening, W. F. Mivelaz and R. F. Crow, with W. G. Hime of Erlin, Hime Associates acting as consultant. The certified value for a constituent is not expected to deviate from the "true" value by more than ±1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ±5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than those uncertainty figures.

Constituent	Percent by Weight	Constituent	Percent by Weight
CaO[a]	66.0_4	Na_2O	0.15
SiO_2	23.0_7	SrO	.09
Al_2O_3	3.2_8	P_2O_5	.24
Fe_2O_3	1.80	Mn_2O_3	.06
SO_3	2.3_8	F	.04
MgO[a]	0.6_7	ZnO	.01
K_2O	.25	Cr_2O_3	.01
TiO_2	.21	Ign. loss	1.6_9
		Total[b]	99.97

[a]If the procedures of ASTM C114 are followed a small amount of CaO will remain in the MgO precipitate. In this case the uncorrected values given below for CaO and MgO should be used.

CaO	66.0_2
MgO	0.6_8

[b]A correction has been made for the amount of fluoride present. This correction, which was subtracted from the gross total, was determined by multiplying the percent fluoride by the ratio of the atomic weight of oxygen to the molecular weight of fluorine (0.421).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by B. E. Foster, R. E. Michaelis, and C. L. Stanley.

Washington, D.C. 20234
December 15, 1983
(Revision of certificates
dated 2-24-77 and 6-12-74)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(Over)

HOMOGENEITY TESTING: Measurements were made at NBS on the portland cement supplied by the Kaiser Cement & Gypsum Corp. by S. D. Rasberry, M. M. Darr, and J. McKay by x-ray fluorescence analysis. The cement was sampled at 16 locations and two briquettes were prepared for each one. Calcium and sulfur, chosen as key elements for checking inhomogeneity, were determined by making four independent measurements on each briquette. A trend-elimination statistical design was employed in measuring the specimens. An analysis of these data indicated the homogeneity was satisfactory. Following these measurements the cement was thoroughly blended and packaged in hermetically sealed glass vials by personnel of the Cement and Concrete Research Laboratory and the Office of Standard Reference Materials.

DEFINITIVE ANALYSIS PROGRAM OF THE PORTLAND CEMENT CORPORATION: "Wet" chemical gravimetric methods were used for the major constituents CaO, SiO_2, Al_2O_3 and MgO. (The methods were essentially those of ASTM C114 using a 0.5-g sample.) Fe_2O_3 was determined by dichromate titration and SO_3 by precipitation in an acid solution after removal of the ammonium hydroxide group and silica. Atomic absorption spectroscopy techniques were used for K_2O, Na_2O, SrO, Mn_2O_3, ZnO and Cr_2O_3. Colorimetric techniques were used to determine TiO_2 and P_2O_5 while fluoride was determined by an ion selective electrode method. Loss on ignition was determined at 1000°C. In each determination duplicate measurements were made on two to ten randomly selected samples. Through the use of various techniques (colorimetric, gravimetric, potentiometric, optical emission elements were determined to be less than 0.01 wt%: Cl, Ba, Zr, B, V, Ni, Mo, Sn, Pb, Cu, and Ag. The total of 99.97 % of the certified constituents in the cement corroborates the evaluation and indicates that significant biases have not been introduced.

CAUTION: To obtain the most accurate results by x-ray fluorescent methods of analysis, the user should compare his samples to the particular SRM that is most nearly the same in overall chemical composition. Alternatively, inter-element effect calibration procedures may be adopted to minimize biases.

U.S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 638

Portland Cement
(Cap Color is Green)

This Standard Reference Material (SRM) is intended for use in checking chemical methods of analysis and in calibration of instrumental methods of analysis.

The value listed for a constituent is the *present best estimate* of the "true" value based on the results of a definitive analysis program carried out in the laboratories of the Portland Cement Association by N. R. Greening, W. F. Mivelaz and R. F. Crow, with W. G. Hime of Erlin, Hime Associates acting as consultant. The certified value for a constituent is not expected to deviate from the "true" value by more than ±1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ±5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than those uncertainty figures.

Constituent	Percent by Weight	Constituent	Percent by Weight
CaO[a]	62.0_9	Na_2O	0.13
SiO_2	21.4_8	SrO	.07
Al_2O_3	4.4_5	P_2O_5	.06
Fe_2O_3	3.55	Mn_2O_3	.05
SO_3	2.3_4	F	.04
MgO[a]	3.8_3	ZnO	.10
K_2O	0.59	Cr_2O_3	.01
TiO_2	.25	Ign. loss	$.9_5$
		Total[b]	99.97

[a]If the procedures of ASTM C114 are foliowed a small amount of CaO will remain in the MgO precipitate. In this case the uncorrected values given below for CaO and MgO should be used.

CaO	62.0_5
MgO	3.8_6

[b]A correction has been made for the amount of fluoride present. This correction, which was subtracted from the gross total, was determined by multiplying the percent fluoride by the ratio of the atomic weight of oxygen to the molecular weight of fluorine (0.421).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by B. E. Foster, R. E. Michaelis, and C. L. Stanley.

Washington, D.C. 20234
December 15, 1983
(Revision of certificates
dated 2-24-77 and 6-12-74)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(Over)

HOMOGENEITY TESTING: Measurements were made at NBS on the portland cement supplied by the Marquette Cement Corporation by S. D. Rasberry, M. M. Darr, and J. McKay by x-ray fluorescence analysis. The cement was sampled at 16 locations and two briquettes were prepared for each one. Calcium and sulfur, chosen as key elements for checking inhomogeneity, were determined by making four independent measurements on each briquette. A trend-elimination statistical design was employed in measuring the specimens. An analysis of these data indicated the homogeneity was satisfactory. Following these measurements the cement was thoroughly blended and packaged in hermetically sealed glass vials by personnel of the Cement and Concrete Research Laboratory and the Office of Standard Reference Materials.

DEFINITIVE ANALYSIS PROGRAM OF THE PORTLAND CEMENT CORPORATION: "Wet" chemical gravimetric methods were used for the major constituents CaO, SiO_2, Al_2O_3 and MgO. (The methods were essentially those of ASTM C114 using a 0.5-g sample.) Fe_2O_3 was determined by dichromate titration and SO_3 by precipitation in an acid solution after removal of the ammonium hydroxide group and silica. Atomic absorption spectroscopy techniques were used for K_2O, Na_2O, SrO, Mn_2O_3, ZnO and Cr_2O_3. Colorimetric techniques were used to determine TiO_2 and P_2O_5 while fluoride was determined by an ion selective electrode method. Loss on ignition was determined at 1000°C. In each determination duplicate measurements were made on two to ten randomly selected samples. Through the use of various techniques (colorimetric, gravimetric, potentiometric, optical emission elements were determined to be less than 0.01 wt%: Cl, Ba, Zr, B, V, Ni, Mo, Sn, Pb, Cu, and Ag. The total of 99.97 % of the certified constituents in the cement corroborates the evaluation and indicates that significant biases have not been introduced.

CAUTION: To obtain the most accurate results by x-ray fluorescent methods of analysis, the user should compare his samples to the particular SRM that is most nearly the same in overall chemical composition. Alternatively, inter-element effect calibration procedures may be adopted to minimize biases.

U.S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 639

Portland Cement
(Cap Color is Clear)

This Standard Reference Material (SRM) is intended for use in checking chemical methods of analysis and in calibration of instrumental methods of analysis.

The value listed for a constituent is the *present best estimate* of the "true" value based on the results of a definitive analysis program carried out in the laboratories of the Portland Cement Association by N. R. Greening, W. F. Mivelaz and R. F. Crow, with W. G. Hime of Erlin, Hime Associates acting as consultant. The certified value for a constituent is not expected to deviate from the "true" value by more than ±1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ±5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than those uncertainty figures.

Constituent	Percent by Weight	Constituent	Percent by Weight
CaO[a]	65.7_6	Na_2O	0.65
SiO_2	21.6_1	SrO	.15
Al_2O_3	4.2_8	P_2O_5	.08
Fe_2O_3	2.40	Mn_2O_3	.08
SO_3	2.4_8	F	.02
MgO[a]	1.2_6	ZnO	.01
K_2O	0.06	Cr_2O_3	.01
TiO_2	.32	Ign. loss	1.0_0
		Total[b]	100.16

[a]If the procedures of ASTM C114 are followed a small amount of CaO will remain in the MgO precipitate. In this case the uncorrected values given below for CaO and MgO should be used.

CaO	65.7_3
MgO	1.2_8

[b]A correction has been made for the amount of fluoride present. This correction, which was subtracted from the gross total, was determined by multiplying the percent fluoride by the ratio of the atomic weight of oxygen to the molecular weight of fluorine (0.421).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by B. E. Foster, R. E. Michaelis, and C. L. Stanley.

Washington, D.C. 20234
December 15, 1983
(Revision of certificates
dated 2-24-77 and 6-12-74)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(Over)

HOMOGENEITY TESTING: Measurements were made at NBS on the portland cement supplied by the Centex Cement Corporation by S. D. Rasberry, M. M. Darr, and J. McKay by x-ray fluorescence analysis. The cement was sampled at 16 locations and two briquettes were prepared for each one. Calcium and sulfur, chosen as key elements for checking inhomogeneity, were determined by making four independent measurements on each briquette. A trend-elimination statistical design was employed in measuring the specimens. An analysis of these data indicated the homogeneity was satisfactory. Following these measurements the cement was thoroughly blended and packaged in hermetically sealed glass vials by personnel of the Cement and Concrete Research Laboratory and the Office of Standard Reference Materials.

DEFINITIVE ANALYSIS PROGRAM OF THE PORTLAND CEMENT CORPORATION: "Wet" chemical gravimetric methods were used for the major constituents CaO, SiO_2, Al_2O_3 and MgO. (The methods were essentially those of ASTM C114 using a 0.5-g sample.) Fe_2O_3 was determined by dichromate titration and SO_3 by precipitation in an acid solution after removal of the ammonium hydroxide group and silica. Atomic absorption spectroscopy techniques were used for K_2O, Na_2O, SrO, Mn_2O_3, ZnO and Cr_2O_3. Colorimetric techniques were used to determine TiO_2 and P_2O_5 while fluoride was determined by an ion selective electrode method. Loss on ignition was determined at 1000°C. In each determination duplicate measurements were made on two to ten randomly selected samples. Through the use of various techniques (colorimetric, gravimetric, potentiometric, optical emission elements were determined to be less than 0.01 wt%: Cl, Ba, Zr, B, V, Ni, Mo, Sn, Pb, Cu, and Ag. The total of 100.16% of the certified constituents in the cement corroborates the evaluation and indicates that significant biases have not been introduced.

CAUTION: To obtain the most accurate results by x-ray fluorescent methods of analysis, the user should compare his samples to the particular SRM that is most nearly the same in overall chemical composition. Alternatively, inter-element effect calibration procedures may be adopted to minimize biases.

U. S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1880

Portland Cement

(Cap Color is Black)

This Standard Reference Material (SRM) is intended for use in evaluating chemical methods of analysis and in the calibration of instrumental methods of analysis. SRM 1880 consists of three sealed vials of type I Portland cement, each containing approximately 5 grams.

The certified value listed for a constituent is the present best estimate of the "true" value based on the results of a definitive analysis program carried out in the laboratories of the Portland Cement Association. The certified value for a constituent is not expected to deviate from the "true" value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than those uncertainty figures.

Constituent	Percent by Weight	Constituent	Percent by Weight
CaO[a]	63.1_4	Na_2O	0.28
SiO_2	19.8_2	SrO	.06
Al_2O_3	5.0_3	P_2O_5	.29
Fe_2O_3	2.91	Mn_2O_3	.08
SO_3	3.37	F	.10
MgO[a]	2.6_9	Cl	.02
K_2O	0.91	ZnO	.01
TiO_2	.23	Ign. loss	1.38
		Total[b]	100.28

[a] If the procedures of ASTM C114 are followed, a small amount of CaO will remain in the MgO precipitate. In this case the uncorrected values given below for CaO and MgO should be used:

CaO	63.0_5
MgO	2.7_5

[b] A correction has been made for the amount of fluoride present. This correction, which was subtracted from the gross total, was determined by multiplying the percent fluoride by the ratio of the atomic weight of oxygen to twice the atomic weight of fluorine (0.421). Correction of the total for the small amount of chloride was negligible (<0.01%).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R.K. Kirby.

Washington, DC 20234
February 10, 1984

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(over)

Acknowledgements

The preparation of this material and the coordination of technical measurements leading to certification were performed under the direction of H.M. Kanare of the Chemical/Physical Research Department, Portland Cement Association (PCA), Skokie, Illinois. The cement was ground and blended with the aid of C. Wilk, J. Leonard, and H. Love. The packaging operations were performed by E. LaBonde, J. Loneard, M. McCann, C. Palmiano, and C. Wilk. Homogeneity testing was performed by C. Palmiano. The definitive analyses were conducted by R. Crow, E. LaBonde, and H. Seiler.

Preparations

This SRM was blended from equal parts of Type I Portland cement supplied by the St. Mary's Cement Company in Canada and the Texas Cement Company. Before blending, each cement was ground in an impact mill until all particles were between 0.5 and 45 μm as selected with an air classifier. The size distributions of the two cements, as determined with a sedimentation apparatus, were quite similar. Tests indicated that after 6 1/2 hours of blending the mix was homogeneous.

Homogeneity Testing

Following the packaging of the cement in hermetically sealed glass vials the homogeneity was determined by measuring 36 samples selected in a stratified random process. X-ray fluorescence analysis was used to determine the differences in calcium, sulfur, and iron by four replicate measurements on each briquette.

Definitive Analysis

"Wet" chemical gravimetric methods were used for the major constituents CaO, SiO_2, Al_2O_3 and MgO. (The methods were essentially those of ASTM C114 using a 0.5-g sample.) Fe_2O_3 was determined by dichromate titration and SO_3 by precipitation in an acid solution. Atomic absorption spectroscopy techniques were used for K_2O, Na_2O, SrO, Mn_2O_3 and ZnO. Colorimetric techniques were used to determine TiO_2 and P_2O_5. Fluoride was determined by an ion selective electrode method and chloride was determined by a potentiometric titration method. Loss on ignition was determined at 1000 °C. In each determination duplicate measurements were made on three to ten randomly selected samples. Through the use of various techniques (colorimetric, gravimetric, and AAS) the presence of the following trace elements were determined to be less than 0.01 wt. %: Ba, Zr, B, and Cr. The total of 100.28% of the certified constituents in the cement corroborates the evaluation and indicates that significant biases have not been introduced.

Caution

To obtain the most accurate results by x-ray fluorescence methods of analysis, the user should compare his samples to the particular SRM's that are most nearly the same in overall chemical composition. Alternatively, interelement effect calibration procedures may be adopted to minimize biases.

National Bureau of Standards

Certificate of Analysis

Standard Reference Material 1881

Portland Cement
(Cap Color is White)

This Standard Reference Material (SRM) is intended for use in evaluating chemical methods of analysis and in the calibration of instrumental methods of analysis. SRM 1881 consists of three sealed vials of type I Portland Cement, each containing approximately 5 grams.

The certified value listed for a constitutent is the present best estimate of the "true" value based on the results of a definitive analysis program carried out in the laboratories of the Portland Cement Association. The certified value for a constituent is not expected to deviate from the "true" value by more than ± 1 in the last significant figure reported; for a subscript figure, the deviation is not expected to be more than ± 5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than those uncertainty figures.

Constituent	Percent by Weight	Constituent	Percent by Weight
CaO^a	58.67	Na_2O	0.04
SiO_2	22.25	SrO	11
Al_2O_3	4.16	P_2O_5	0.09
Fe_2O_3	4.68	Mn_2O_3	0.26
SO_3	3.65	F	0.09
MgO^a	2.63	Cl	0.01
K_2O	1.17	Ign. loss	2.01
TiO_2	0.25	$Total^b$	100.04
ZnO	0.01		

[a] If the procedures of ASTM C114 are followed, a small amount of CaO will remain in the MgO precipitate. In this case the uncorrected values given below for CaO and MgO should be used:

CaO	58.65
MgO	2.70

[b] A correction has been made for the amount of fluoride present. This correction, which was subtracted from the gross total, was determined by multiplying the percent fluoride by the ratio of the atomic weight of oxygen to twice the atomic weight of fluorine (0.421).

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by R.L. McKenzie.

Gaithersburg, MD 20899
December 7, 1987
(Revision of certificate
dated 2-10-84)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(over)

Acknowledgements

The preparation of this material and the coordination of technical measurements leading to certification were performed under the direction of H.M. Kanare of the Chemical/Physical Research Department, Portland Cement Association (PCA), Skokie, Illinois. The cement was ground and blended with the aid of R. Monger. The packaging operations were performed by M. McCann, R. Monger, C. Palmiano, and C. Wilk. Homogeneity testing was performed by J. Leonard and C. Palmiano. The definitive analyses were conducted by R. Crow and H. Seiler.

Preparations

This SRM was blended from a Portland cement supplied by the Portland Cement Association and 5 wt. % of Terra Alba gypsum. Before blending, the cement was ground in an impact mill until all particles were smaller than 40 μm as selected with an air classifier and the gypsum was ground in a steel-ball mill to pass a 200-mesh sieve (<75μm). Tests indicated that after blending the mix was sufficiently homogeneous.

Homogeneity Testing

Following the packaging of the cement in hermetically sealed glass vials the homogeneity was determined by measuring 36 samples selected in a stratified random process. X-ray fluorescence analysis was used to determine the differences in calcium, sulfur, and iron by four replicate measurements on each briquette.

Definitive Analysis

"Wet" chemical gravimetric methods were used for the major constituents CaO, SiO_2, Al_2O_3 and MgO. (The methods were essentially those of ASTM C114 using a 0.5-g sample.) Fe_2O_3 was determined by dichromate titration and SO_3 by precipitation in an acid solution. Atomic absorption spectroscopy techniques were used for K_2O, Na_2O, SrO, Mn_2O_3 and ZnO. Colorimetric techniques were used to determine TiO_2 and P_2O_5. Fluoride was determined by an ion selective electrode method. Loss on ignition was determined at 1000 °C. In each determination duplicate measurements were made on three to ten randomly selected samples. Through the use of various techniques (colorimetric, gravimetric, and AAS) the presence of the following trace elements were determined to be less than 0.01 wt. %: Ba, Zr, B, Cl, and Cr. The total of 100.04% of the certified constituents in the cement corroborates the evaluation and indicates that significant biases have not been introduced.

Caution

To obtain the most accurate results by x-ray fluorescence methods of analysis, the user should compare his samples to the particular SRM's that are most nearly the same in overall chemical composition. Alternatively, interelement effect calibration procedures may be adopted to minimize biases.

Appendix B

Summaries of the homogeneity tests for
SRMs 633
634
635
636
637
638
639
1880
1881
are given in this appendix.

The tests on the "600 series" cements were made by measuring the variation of calcium and sulfur with normal x-ray fluorescence methods using the "1000 series" cements as standards. The packaged vials of each cement were stored in 15 or 16 cans and two vials were taken from each can totaling 30 or 32 specimens. Each specimen were prepared by briquetting. All of these specimens were satisfactory except one from SRM 639 which proved to be defective and was not included in the results. The following tables indicate the average value of four measurements for each element on each specimen. The run-order of the measurements used a trend elimination sequence. Because an analysis on the two vials from each can did not indicate they were "duplicates", each vial was considered to be an independent sample.

The tests on SRMs 1880 and 1881 were made by measuring the variation of calcium, sulfur, and iron with normal x-ray fluorescence methods. Thirty-six vials of each cement were selected in a stratified random process from the cases in which they were stored. A specimen from each vial was prepared by briquetting and four measurements were made for each element. Using one of the specimens as a machine standard, the others were measured using a trend elimination sequence. The following tables indicate the average value of four measurements for each element on each specimen.

SRM 633

CaO		SO_3	
64.95% by wt.	64.87% by wt.	2.181% by wt.	2.206% by wt.
64.97	65.09	2.180	2.191
64.90	65.09	2.215	2.229
64.98	65.06	2.208	2.208
64.97	65.02	2.196	2.232
65.01	64.99	2.218	2.214
64.92	65.19	2.194	2.176
65.06	65.00	2.177	2.189
65.06	64.93	2.197	2.200
65.03	65.02	2.192	2.203
64.88	65.04	2.202	2.195
65.05	64.91	2.194	2.202
65.01	64.99	2.192	2.190
64.95	64.97	2.189	2.209
65.03	65.05	2.205	2.217
64.96	65.05	2.178	2.221

Average	65.00% by wt.	2.200% by wt.
Std. Dev.	0.069% by wt.	0.015% by wt.
Coef. of Var.	0.105%	0.67%

SRM 634

CaO		SO_3	
63.20% by wt.	63.21% by wt.	2.180% by wt.	2.183% by wt.
63.16	63.22	2.200	2.194
63.19	63.29	2.181	2.189
63.29	63.13	2.200	2.192
63.21	63.29	2.193	2.196
63.13	63.18	2.180	2.199
63.18	63.14	2.203	2.211
63.12	63.20	2.204	2.220
63.22	63.22	2.195	2.201
63.22	63.23	2.212	2.191
63.09	63.23	2.191	2.227
63.15	63.12	2.227	2.193
63.25	63.22	2.213	2.206
63.23	63.17	2.204	2.195
63.21	63.33	2.215	2.205
63.13	63.25	2.194	2.204

Average	63.20% by wt.	2.200% by wt.
Std. Dev.	0.057% by wt.	0.012% by wt.
Coef. of Var.	0.091%	0.56%

SRM 635

CaO		SO_3	
59.54% by wt.	59.47% by wt.	6.795% by wt.	6.827% by wt.
59.72	59.80	6.778	6.803
59.90	59.69	6.774	6.777
59.73	59.78	6.814	6.798
59.88	59.83	6.748	6.772
59.65	59.79	6.803	6.814
59.70	59.59	6.842	6.794
59.69	59.71	6.782	6.837
59.68	59.72	6.803	6.835
59.67	59.68	6.776	6.824
59.62	59.53	6.778	6.824
59.61	59.73	6.870	6.779
59.67	59.70	6.752	6.820
59.78	59.64	6.778	6.845
59.68	59.76	6.774	6.804
59.77	59.72	6.784	6.798

Average	59.70% by wt.	6.800% by wt.
Std. Dev.	0.094% by wt.	0.028% by wt.
Coef. of Var.	0.158%	0.40%

SRM 636

CaO		SO_3	
63.91% by wt.	63.89% by wt.	2.193% by wt.	2.189% by wt.
63.81	64.20	2.178	2.180
63.94	63.74	2.158	2.209
63.76	63.85	2.192	2.213
63.84	63.69	2.195	2.220
63.82	63.91	2.179	2.213
63.75	63.81	2.206	2.191
63.80	63.87	2.203	2.196
63.77	63.74	2.206	2.198
63.78	63.63	2.201	2.212
63.66	63.68	2.199	2.213
63.72	63.62	2.224	2.225
63.74	63.85	2.183	2.160
63.84	63.83	2.217	2.236
63.74	63.81	2.183	2.230

Average	63.80% by wt.	2.200% by wt.
Std. Dev	0.111% by wt.	0.019% by wt.
Coef. of Var.	0.176%	0.82%

SRM 637

CaO		SO_3	
66.34% by wt.	66.48% by wt.	2.428% by wt.	2.397% by wt.
66.36	66.47	2.407	2.401
66.40	66.39	2.399	2.405
66.37	66.45	2.392	2.420
66.44	66.54	2.391	2.407
66.27	66.40	2.404	2.406
66.35	66.22	2.415	2.412
66.42	66.46	2.385	2.387
66.53	66.27	2.407	2.398
66.46	66.32	2.401	2.394
66.54	66.30	2.382	2.403
66.52	66.30	2.399	2.398
66.40	66.49	2.381	2.401
66.39	66.42	2.402	2.378
66.35	66.34	2.400	2.400
Average	66.40% by wt.		2.400% by wt.
Std. Dev.	0.085% by wt.		0.011% by wt.
Coef. of Var.	0.129%		0.47%

SRM 638

CaO		SO_3	
62.15% by wt.	62.07% by wt.	2.400% by wt.	2.423% by wt.
62.15	62.24	2.363	2.397
62.15	62.00	2.415	2.413
62.06	62.12	2.408	2.402
62.13	62.10	2.410	2.402
61.96	62.09	2.396	2.381
62.31	62.17	2.389	2.365
62.06	62.15	2.392	2.393
62.09	62.02	2.398	2.389
62.08	61.98	2.384	2.420
62.08	62.14	2.414	2.413
61.97	62.10	2.423	2.387
62.11	62.06	2.414	2.425
62.01	62.21	2.380	2.396
62.05	62.16	2.402	2.406
Average	62.10% by wt.		2.400% by wt.
Std. Dev.	0.077% by wt.		0.016% by wt.
Coef. of Var.	0.124%		0.68%

SRM 639

CaO		SO_3	
66.64% by wt.	66.75% by wt.	2.527% by wt.	2.502% by wt.
66.49	66.66	2.475	2.519
66.54	66.67	2.520	2.498
66.70	66.53	2.503	2.503
66.33	66.65	2.525	2.509
66.71	66.57	2.492	2.514
66.46	66.52	2.475	2.514
66.66	66.45	2.478	2.534
66.38	66.62	2.532	2.500
66.59	66.40	2.487	2.531
66.47	66.60	2.525	2.532
66.62	66.44	2.490	2.539
66.49	66.58	2.522	2.542
66.35	66.41	2.515	2.487
66.46		2.513	

Average	66.50% by wt.	2.500% by wt.
Std. Dev.	0.115% by wt.	0.020% by wt.
Coef. of Var.	0.175%	0.79%

SRM 1880

	CaO	SO_3	Fe_2O_3
	63.11% by wt.	3.338% by wt.	2.809% by wt.
	63.52	3.332	2.814
	63.02	3.371	2.802
	63.12	3.361	2.807
	63.17	3.324	2.810
	63.25	3.361	2.828
	63.22	3.334	2.817
	63.16	3.355	2.809
	63.08	3.381	2.807
	63.27	3.365	2.811
	62.88	3.353	2.796
	63.14	3.381	2.812
	62.94	3.343	2.811
	63.34	3.368	2.808
	63.10	3.362	2.826
	63.04	3.326	2.826
	63.06	3.356	2.800
	63.08	3.301	2.802
	63.12	3.349	2.811
	63.07	3.328	2.814
	63.16	3.347	2.806
	62.98	3.359	2.805
	63.14	3.353	2.803
	63.02	3.376	2.804
	63.14	3.353	2.816
	63.58	3.374	2.818
	62.89	3.358	2.814
	63.42	3.332	2.827
	63.01	3.321	2.794
	63.08	3.310	2.803
	63.18	3.360	2.818
	63.03	3.364	2.807
	63.39	3.355	2.812
	63.27	3.327	2.804
	62.84	3.327	2.791
Average	63.14% by wt.	3.349% by wt.	2.810% by wt.
Std. Dev.	0.168% by wt.	0.021% by wt.	0.0089% by wt.
Coef. of Var.	0.265%	0.60%	0.32%

SRM 1881

CaP	SO_3	Fe_2O_3
60.14% by wt.	3.869% by wt.	5.007% by wt.
59.99	3.681*	4.970
60.11	3.833	4.984
59.98	3.824	4.990
60.06	3.864	4.980
60.03	3.868	4.993
60.05	3.858	5.011
60.01	3.875	4.994
60.12	3.862	4.998
60.04	3.796	4.970
59.95	3.841	4.975
59.93	3.856	4.981
60.34	3.756	4.988
60.16	3.881	4.997
60.15	3.886	5.010
59.93	3.829	4.985
60.16	3.754	4.996
60.27	3.896	4.998
60.10	3.789	4.997
59.92	3.820	5.002
59.95	3.873	4.982
59.77	3.773	4.969
60.06	3.881	4.993
59.96	3.860	4.973
60.09	3.837	4.999
60.15	3.843	4.997
59.84	3.790	4.970
59.95	3.780	4.981
59.95	3.792	4.974
59.92	3.833	4.984
60.04	3.827	4.989
59.98	3.841	4.989
60.12	3.851	4.997
60.14	3.823	4.985
60.08	3.774	4.986
Average 60.04% by wt.	3.833% by wt.	4.988% by wt.
Std. Dev. 0.115% by wt.	0.039% by wt.	0.0116% by wt.
Coef. of Var. 0.193%	1.02%	0.23%

*Value not included in the statistics.

Appendix C

Results of the Cooperative Test Program for the Chemical Analysis of SRMs 633 through 639

PARTICIPATING LABORATORIES

Atlantic Cement Co.
P.O. Box 3
Ravena, NY 12143
Methods (W,F,J)

Ash Grove Cement Co.
640 Southwest Blvd.
Kansas City, KS 66103
Methods (X,A)

California Portland Cement Co.
P.O. Box 947
Colton, CA 92324
Methods (W,F,A)

Capitol Cement
P.O. Box 412
San Antonio, TX 78218
Methods (W,A)

Department of the Army
Waterways Experiment Station
Corps of Engineers
P.O. Box 631
Vicksburg, MS 39180
Methods (W,F)

Marquette Cement
20 North Wacker Drive
Chicago, IL 60606
Methods (W,F,C)

National Bureau of Standards
Analytical Chemistry Division
Gaithersburg, MD 20899
Method (X)

Pacific Western Ind., Inc.
P.O. Box 1247
Lebec, CA 93243
Methods (W,A,C)

Penn-Dixie Cement Corp.
P.O. Box 152
Nazareth, PA 18064
Method (X)

Portland Cement Association
5420 Old Orchard Road
Skokie, IL 60077
Methods (W,J,A,C)

Southwestern Portland Cement Co.
P.O. Box 937
Victorville, CA 92392
Method (X)

St. Mary's Cement Co. Ltd.
P.O. Box 68
Bowmanville, Ontario
Canada
Methods (W,F,C)

Universal Atlas Cement
Buffington Station
Gary, IL 46401
Methods (J,F)

A summary of the results of the cooperative test program is given in Table C. The complete data of this program as reported by William G. Hine of Erlin, Hine Associates is available from the National Bureau of Standards, Office of Standard Reference Materials. The code for the methods used in this program are as follows:

A Atomic Absorption
C Colorimetry
F Flame Photometry
J Jugovic
W Wet
X X-Ray Fluorescence

The deviations reported in the table were determined by

$$\frac{1}{7}\sum\left[\frac{1}{n}\sum_{i}^{n} x_i - x_{cert}\right]$$

where x_i are the n individual measurements made on each of the seven cements and x_{cert} are the final certified values for that component. The ranges are determined by

$$\left[\frac{1}{n}\sum_{i}^{n} x_i - x_{cert}\right]_{max} - \left[\frac{1}{n}\sum_{i}^{n} x_i - x_{cert}\right]_{min}$$

The values for the deviations and ranges for SO_3 as determined by x-ray fluorescence do not include the values obtained on SRM 635 (~7% SO_3) for which the deviations reached 1.8%.

A copy of the preliminary certificate that was based on the results of this program is also provided.

Table C-1. Summary of the Cooperative Test Program on the "600 Series" SRMs, % by wt.

	CaO			SiO_2			Al_2O_3			Fe_2O_3			SO_3			MgO	
Lab	Method	Deviation	Range	Method	Deviation	Range	Method	Deviation	Range	Method	Deviation	Range	Method	Deviation	Range	Method	Deviation	Range
7	W	0.0	0.3	W	-0.07	0.08	W	+0.1	0.2	W	+0.02	0.03	W	-0.04	0.07	W	+0.10	0.14
8	W	0.0	0.4	W	-0.18	0.13	W	0.0	0.1	W	+0.08	0.20	W	-0.08	0.12	W	+0.06	0.20
12	W	0.0	0.6	W	0.00	0.36	W	-0.1	0.2	W	+0.04	0.05	W	-0.01	0.12	W	+0.07	0.28
5	W	0.0	0.1	W	+0.10	0.08	W	0.0	0.4	W	0.00	0.02				W	+0.04	0.04
1	W	+0.2	0.2	W	-0.13	0.09	W	+0.3	0.3	W	+0.16	0.07	W	-0.06	0.09	W	-0.04	0.08
4	W	-0.2	0.3	W	-0.03	0.37	W	+0.1	0.2	W	-0.04	0.05	W	-0.06	0.12	W	+0.08	0.15
13	W	+0.2	0.4	W	+0.09	0.28	W	-0.2	0.3	W	+0.11	0.12	W	-0.04	0.12	W	-0.04	0.21
6	W	+0.4	0.9	W	-0.09	0.39	A	-0.1	0.4	A	+0.11	0.09	W	-0.20	0.18	A	+0.01	0.18
5	A	0.0	0.2	A	+0.10	0.08	A	0.0	0.3	A	+0.02	0.04	W	-0.01	0.06	A	+0.05	0.06
10	J	+0.1	0.3	J	-0.02	0.25	J	-0.1	0.4	J	0.00	0.07	J	+0.01	0.14	J	+0.06	0.20
2	X	+0.2	0.6	X	+0.20	1.09	X	+0.1	0.2	X	+0.04	0.18	X	+0.02	0.13	X	+0.16	0.57
11	X	-0.3	0.6	X	+0.17	0.54	X	+0.1	0.5	X	+0.15	0.36	X	-0.11	0.11	X	+0.32	0.29
3	X	-0.1	0.7	X	-0.18	0.57	X	-0.1	0.4	X	+0.11	0.22	X	-0.24	0.08	X	-0.09	0.23
9	X	+0.4	1.1	X	-0.03	1.14	X	+0.1	0.6	X	+0.04	0.13	X	-0.09	0.51			
1	X	+0.2	0.5	X	+0.09	0.79	X	0.0	0.3	X	+0.03	0.18	X	-0.04	0.22	X	-0.03	0.25
8	X	+0.1	0.7	X	-0.16	0.52	X	0.0	0.2	X	+0.14	0.14	X	0.00	0.06	X	+0.12	0.37
12	X	+0.5	1.7	X	+0.12	0.64	X	+0.1	0.5	X	-0.03	0.24	X	+0.08	0.14	X	+0.05	0.24

Table C-1. (Continued)

	K_2O			TiO_2			Na_2O			SrO			P_2O_5			Mn_2O_3			Ign Loss	
Lab	Method	Deviation	Range	Method	Deviation	Range	Method	Deviation	Range	Method	Deviation	Range	Method	Deviation	Range	Method	Deviation	Range	Method	Deviation
7	F	-0.01	0.04	W	0.00	0.02	F	-0.01	0.04				W	0.00	0.02	W	-0.01	0.01	+0.01	0.07
8	F	0.00	0.07	C	-0.01	0.05	F	-0.07	0.16	W	0.00	0.23	W	0.00	0.01	W	-0.01	0.02	+0.05	0.28
12	F	0.00	0.03	J	-0.02	0.02	F	-0.01	0.02				J	0.00	0.01	W	+0.01	0.03	+0.06	0.07
5																				
1	F	+0.01	0.03	C	-0.03	0.05	F	+0.01	0.06				C	+0.01	0.08	W	+0.01	0.13	+0.04	0.11
4	F	-0.01	0.04	A	0.00	0.08	F	0.00	0.07	A	+0.02	0.03	W	0.00	0.01	A	+0.03	0.09	+0.02	0.13
13	A	0.00	0.10	C	-0.02	0.17	A	-0.04	0.09				C	-0.04	0.13	C	+0.02	0.04	-0.02	0.10
6	A	0.00	0.03	A	-0.06	0.16	A	-0.01	0.04	A	0.00	0.03	W	+0.03	0.14	A	0.00	0.03	+0.01	0.14
5	A	0.00	0.03	J	0.00	0.01	A	0.00	0.01	A	0.00	0.01	C	0.00	0.01	A	0.00	0.00	0.00	0.02
10	F	-0.01	0.05	J	+0.01	0.03	F	+0.01	0.04				J	0.00	0.01	J	0.00	0.03	-0.02	0.10
2	X	+0.01	0.03	X	0.00	0.03	A	-0.01	0.08	X	0.00	0.04	X	+0.01	0.08	X	0.00	0.02	+0.04	0.14
11	X	+0.03	0.20	X	+0.01	0.05	X	+0.05	0.18	X	-0.01	0.02							+0.03	0.14
3	X	+0.03	0.05	X	0.00	0.07							X	-0.08	0.06					
9	X	+0.01	0.06	X	0.00	0.01				X	0.00	0.03	X	+0.01	0.03	X	+0.01	0.07		
1	X	0.00	0.02	X	0.00	0.04							X	+0.03	0.05					
8	X	-0.01	0.04	X	-0.01	0.03				X	+0.01	0.01								
12	X	+0.01	0.05																	

U. S. Department of Commerce
Frederick B. Dent
Secretary

National Bureau of Standards
Richard W. Roberts, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Materials 633-639

Portland Cements

These SRM's are fine powders and are intended for use both in checking chemical methods of analysis and in calibration with instrumental methods of analysis.

SRM No.	633	634	635	636	637	638	639
CAP COLOR	RED	GOLD	BLUE	YELLOW	PINK	GREEN	CLEAR
Constituent	Percent by Weight						
Al_2O_3	3.7_4	5.2	6.2	3.1	3.3	4.5	4.3
CaO	$64._5$	$62._6$	$59._8$	$63._5$	$66._0$	$62._1$	$65._8$
MgO	1.0_4	3.4	1.2_5	4.0	0.7_2	3.8_4	1.2_9
TiO_2	0.24	0.30	0.32	0.17	.21	0.25	0.31
SiO_2	21.9	20.7	18.5	23.2	23.1	21.4	21.6
SO_3	2.1_8	2.1_6	7.0	2.3	2.3_3	2.3	2.4
P_2O_5	0.24	0.10	0.17	0.09	0.25	0.06	0.08
Mn_2O_3	.04	.28	.09	.12	.06	.05	.08
K_2O	$.16_5$	.43	.45	.57	$.24_5$	.59	.05
Na_2O	$.6_4$	.14	.07	.10	.13	.12	$.6_7$
SrO	.31	.12	.22	.04	.10	.07	.15
Fe_2O_3	4.2	2.8_7	2.6_5	1.6_2	1.8_0	3.5_8	2.4_2
Ign. loss	0.7_5	1.6_1	3.2_5	1.1_6	1.6_8	0.9_5	1.0
Total	99.95	99.91	99.97	99.97	99.93	99.81[a]	100.13

[a] One laboratory reported 0.11 ZnO in this SRM, thus increasing the total to 99.92%.

PRELIMINARY CERTIFICATION: This Certificate is "preliminary" because additional analytical work is planned that will improve the accuracy of some of the values listed. The value listed for a constituent is the present best estimate of the "true" value based on the results of the analytical program. The values are not expected to deviate from the "true" values by more than ±1 in the last significant figure reported; for subscript figures, the deviation is not expected to be more than ±5. Based on the results of homogeneity testing, maximum variations within and among samples are estimated to be less than the uncertainty figures given above.

Washington, D.C. 20234
June 12, 1974

J. Paul Cali, Chief
Office of Standard Reference Materials

Appendix D

Letter sent to members of ASTM Committee C-1 soliciting their help in selecting the new SRMs.

Dear ASTM Member:

Two new portland cement chemical standard reference materials are being produced by the Portland Cement Association for the National Bureau of Standards. These will supplement the seven samples currently available from NBS (SRM 633-639).

We would like to know what chemical composition you think these new standard cements should have. For your reference, we have attached a copy of the Certificate of Analysis for SRM 633-639. Please write your suggestions for the proposed cement standards below the certified values, and return to:

Howard Kanare
NBS Cement Standards Project
Portland Cement Association
5420 Old Orchard Road
Skokie, Illinois 60077

We would appreciate your reply before March 15, 1981. Thank you for your suggestions.

Sincerely,

R. F. Gebhardt
Chairman
C-01.23 on Chemical Analysis

Appendix E

List of Equipment and Packaging Materials Used in Preparing SRMs 1880 and 1881.

Vortec Impact Mill, Model M-1
Vortec Air Classifier, Model C-14
Micromeritics Sedi-Graph Particle Size Analyzer
Paul O. Abbe Steel-Ribbon Blender, Model 7
Mateer-Burt Auger-Type Power Filler, Model 31-A
Kimble Type III Flint-Glass Flat-Bottom Shell Vial
(15-mm O.D. x 45-mm height)
TLB Plastics Corp. High-Density Polyethylene Cap
(fits one dram shell vial)
Kimble Type III Flint-Glass Flat-Bottom Shell Vial
(19-mm O.D. x 100-mm height)
Glass Fiber Pad (Filter Disc)
(12.5-mm dia. x 0.5-mm thick)
Flame Sealing Machine (NBS Property)
Rigaku XRF Spectrometer, Model 306/
X-Rays: 40-kv, 70-mA water-cooled rhodium target tube fitted with a Rh-plated beam defining cone.
Sample: Pressed powder briquet, 30 x 3 mm in aluminum cap, pressed at 50,000 psi, spining sample holder with 25-mm diameter copper mask.

Element	Crystal	Line	Detector	Counting Time	Typical Counts Per Measurement
Ca	LiF(200)	K	FPC*	20 sec.	510,000
Fe	LiF(200)	K	SC	40 sec.	260,000
S	Ge	K	FPC*	20 sec.	240,000

*Flow Proportional Counter with P-10 gas at 0.05 scfh.

Cardboard Shipping Boxes and Trays (285 vials per tray)

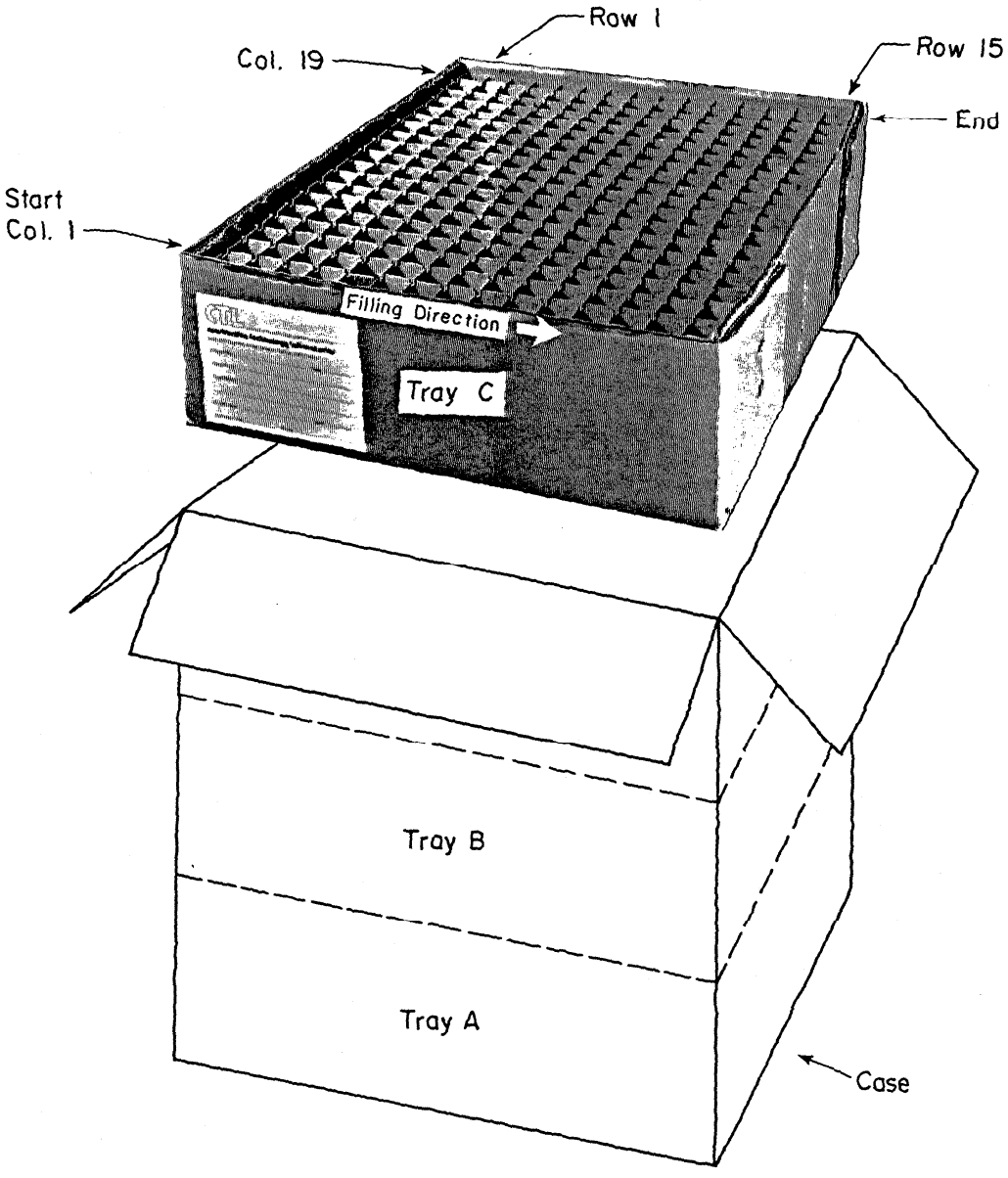

Figure E-1. Packing case for SRMs 1880 and 1881

Appendix F

Some miscellaneous information is provided in this appendix including values for the Blaine surface area given in Table F1.

Table F1. Blaine Surface Area*

SRM	Average	n	Std Dev
633	3015 cm^2/g	3	32 cm^2/g
634	3485	3	144
635	4840	3	122
636	3609	3	88
637	5678	3	134
638	3735	3	49
639	3356	3	76
1016	3305	3	46

*Data reported by Norman H. Suhr of the Pennsylvania State University.

Table F2. Chemical Analysis of the SRM 1880 Cements Before Blending, % by wt.

	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O
Cement A	61.31	20.25	4.30	3.12	3.73	4.33	0.98	0.58
Cement B	64.24	19.63	5.64	2.86	3.21	1.13	0.91	0.13

NOTE: All analyses by x-ray fluorescence

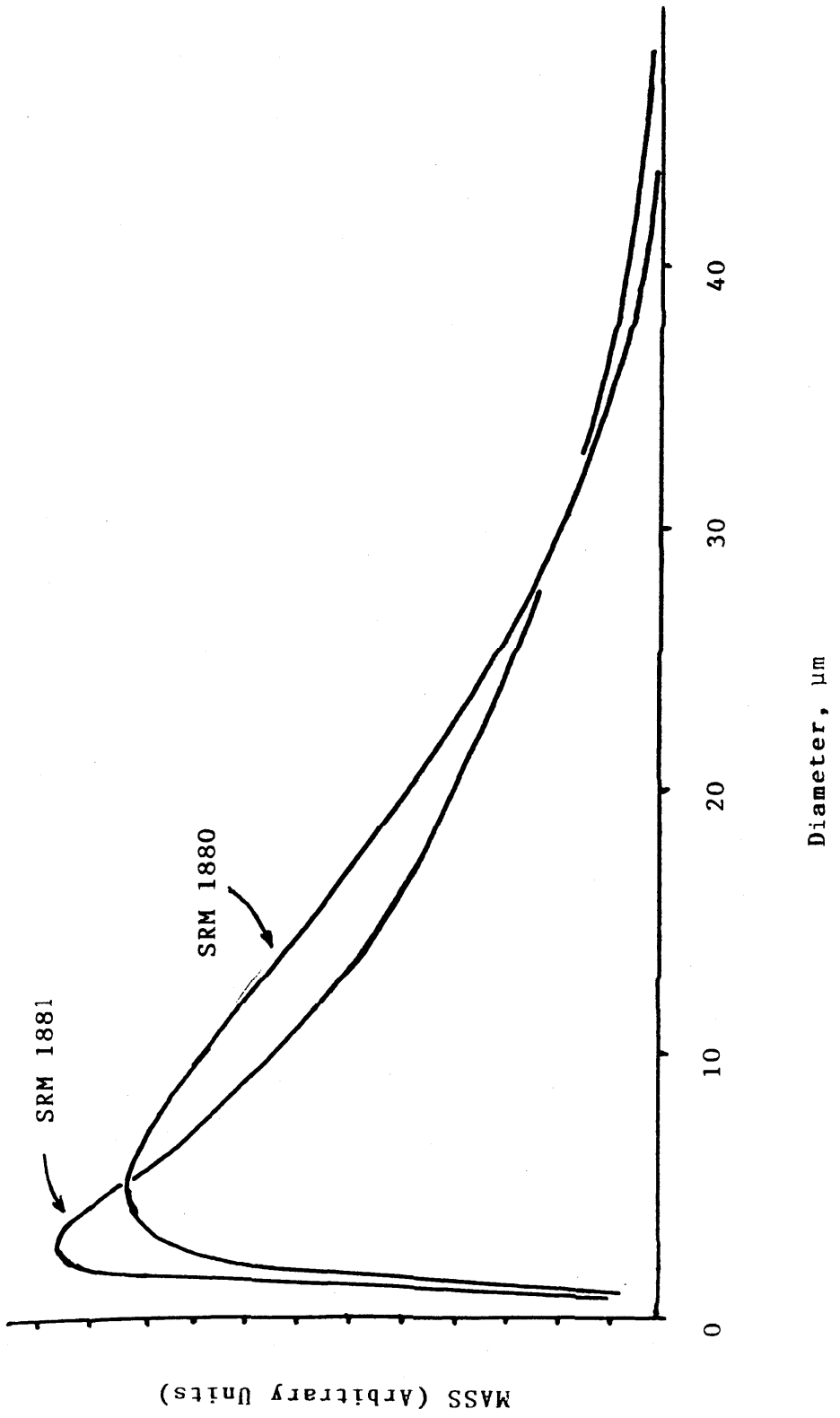

Figure F-1. Results of particle size analysis of SRMs 1880 and 1881.

Appendix G

Flexible Packaging Study*

The intent of this study was to determine if modern flexible packages could preserve the properties of cement. Such packages are widely used for the storage of foodstuffs, medicine, and electronic equipment.

The potential advantages of flexible packages include:

(1) high speed filling and sealing;
(2) low-volume storage compared to glass;
(3) reduced weight;
(4) reduced breakage in shipping and handling;
(5) ease of shipping through automated labelling; and
(6) ease of identification through prelabelling.

Water vaporproof flexible packages generally are composed of several laminations of different materials, each serving a specific function. A schematic of a typical laminated film is shown in Figure G1. These layers can be coextruded (dry lamination) or, more commonly, attached

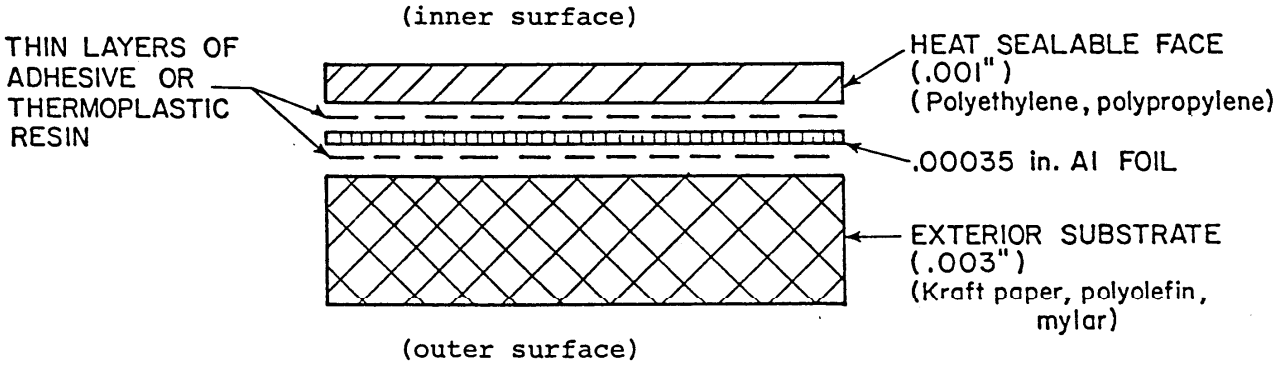

Figure G1. Schematic of typical laminated film

with thin layers of adhesives. The outer substrate provides mechanical strength, abrasion resistance, and a surface for labelling. The aluminum foil is the actual barrier to moisture and gas transmission. The heat-sealable face can be any number of thermoplastic materials, usually polyethylene, polypropylene, or a proprietary plastic film.

*Conducted by PCA under contract to NBS.

The plan of this investigation was to encase portland cement samples in various types of commercially available flexible packages and then test them under average conditions including heat, moisture, high CO_2, and mechanical abuse. The contents of the packages would then be analyzed for changes by measuring properties such as specific surface area and ignition loss. The packages would be examined for degradation, including maceration, delamination, splitting or cracking, and discoloration.

A commonly used military specification (MIL-B-131E) was considered as a general guide to the testing of the flexible packages. This specification lists the required physical properties for a packaging material to be qualified as a "water vaporproof, flexible, heat-sealable, barrier material". However, the determination of the maximum permissible water vapor transmission rate (WVTR) as required in this specification would not be an acceptable test for the protection of cement. Therefore, modifications of the test procedures were imposed to evaluate the various types of flexible packages under extremely adverse conditions.

Eight types of flexible packaging films were made available for testing. Six to twelve pouches were made from each film, filled with approximately 15 g of portland cement, and heat sealed. The descriptions of the packets are given in Table G1.

One or two samples of each type of package were placed into each of the environmental chambers listed below:

A. Fog Room (73 °F and 100% R.H.). Packages placed on a wire mesh shelf.
B. High CO_2 Atmosphere (73 °F, 71% R.H., and 100% CO_2).
   Packages placed on a wire mesh shelf above saturated ($SrCl_2 \cdot 6H_2O$) solution inside a 3-liter glass jar.
   Note: This humidity is nearly the optimum for carbonation of cement.
C. Hot Room (100 °F and 20% R.H.). Packages placed in loosely covered cardboard box.
D. Cold Room (0 °F). Packages placed in loosely covered cardboard box.

Packages remained in these chambers for 14 to 28 days. They were then removed and inspected. The packages that did not appear badly degraded were then opened and the cements were tested for ignition loss in accordance with ASTM C114. Tests for specific surface area using the Blaine Air Permeability apparatus were found to be not sensitive enough to serve as an indicator of changes in cement properties.

Table G-1. Description of Flexible Packages as Received

ID#	Outer Substrate	Barrier	Inner Sealing Film	Empty Package Weight (3-1/2"x5")[a]	Appearance
1	Saran/nylon	Saran/nylon	Polyethylene	2.5 g	Smooth, transparent fairly flexible
2	White Kraft paper	Foil	Polyethylene	3.1 g	Semi-gloss, smooth, opaque, stiff
3	Brown Kraft paper	Foil	Polyethylene	4.4 g	Matte finish, opaque, stiff
4	Tyvek (TM) Polyolefin	Foil	Polyethylene	3.9 g	Opaque, white, semi-gloss, stiff
5	Brown Kraft paper	-	Polyethylene	2.7 g	Matte finish, opaq fairly flexible
6	Mylar (TM)	Foil/ Mylar(TM)	Polyethylene	3.4 g	Silver, glossy, opaque, fairly, stiff
7	Gold lacquer/ Mylar(TM)	Metallized nylon	Polyethylene	1.4 g	Glossy, gold, opaque, very flexible
8	White Kraft paper	Foil	Surlyn(TM)	3.9 g	Semi-gloss, opaque fairly stiff

[a]For reference, an empty glass vial and cap as used for the cement SRMs weighed about 14.0 g.

Table G-2. Appearance of Packages After Tests

Package ID	Test A (Fog Room)	Test C (Hot Room)	Test D (Cold
1	Severe delamination of Saran; all-around edge curl; slight discoloration	Slight edge curl; slight discoloration	Appearance as received
2	Slight maceration; very slight edge curl; no delamination	Appearance as received	Very slight e curl
3	Some staining; no edge curl; some wrinkles no delamination	Appearance as received	Appearance as received
4	Appearance as received	Appearance as received	Appearance as received
5	Slight maceration; some staining; some wrinkling	Appearance as received	Appearance as received
6	Appearance as received	Appearance as received	Appearance as received
7	Major edge curl; severe delamination of gold-lacquered top layer	Slight edge curl	All-around ed curl
8	Minor edge curl, some wrinkling no discoloration	Appearance as received	Moderate edge

Selected packages from Test C (Hot Room) were opened and the cement extracted with hot $CHCl_3$ using a procedure previously developed at PCA. The weights of the $CHCl_3$-soluble residues were determined and their infrared spectra were recorded.

To measure resistance to physical abuse, selected packages were attached to a high-speed vibrating table (Syntron Jogger J-1A) for about six hours. The two sides of the packages were then separated by cutting just inside all four seams, and the inner surfaces were rubbed together with cement in between to abrade the heat-sealable films. These inner surfaces were then cleaned by swabbing with alcohol, and examined by scanning electron microscopy. A glass vial containing cement was similarly vibrated and examined for comparison.

The appearances of the packages after removal from test chambers A, C, and D are given in Table G2. Packages 1 and 7 were badly delaminated after Test A. All other packages appeared good although the paper layers were slightly macerated. Ignition losses were measured for all packages after removal from test chamber A following two days of drying at 73 °F and 40% R.H. The results of these tests are given in Table G3. After analyzing these results and considering their appearance, Packages 1, 3, 5, and 7 were eliminated from further consideration.

Table G3. Effect of High Humidity

Package	Ignition Loss	Package	Ignition Loss
Control	0.72% by wt.	5	1.37% by wt.
1	2.00	6	0.71
2	0.71	7	0.89
3	0.99	8	0.67
4	0.72		

Packages 2, 4, 6, and 8 were removed from test chamber B and after drying, ignition losses were determined. See Table G4.

Table G4. Effect of High CO_2 Atmosphere

Package	Ignition Loss
2	0.66% by wt.
4	0.68
6	0.72
8	0.68

All of these packages appeared to prohibit carbonation of the cement under the conditions of the test, and should therefore be considered good barriers to the transmission of moisture and CO_2 at room temperatures. Packages having polyethylene and Surlyn(TM) as the inner heat sealable surface were removed from test chamber C and conditioned at 73 °F and 40% R.H. for two days before the cement was extracted with $CHCl_3$. The weights of the $CHCl_3$-soluble residues are given in Table G5. Infrared spectra of the top two residues indicated only hydrocarbons in the cements, typical of trace residues found in commercial

portland cements. The infrared spectrum of the residue from Package 8 was complex, indicating the presence of short chain esters and amides. These are degradation products of the polymer and the "slip additive" which permits manipulation of Surlyn(TM) by high-speed machines.

Table G5. Effect of Hot Environment

Package	Residue
Control	0.006%
3	0.005
8	0.020

Packages of types 2 and 8 along with a glass vial of SRM 114n were subjected to the vibration and abrasion tests previously described. The external appearance of all three types of containers was unremarkable after the vibration test. Before testing, both the polyethylene and glass had very smooth surfaces showing only minor topography at moderate magnification. The Surlyn(TM) had a cratered appearance that turned out to be caused by the mirror-pocket casting rollers used in extruding this material. After testing and cleaning with alcohol the inner surface of the polyethylene was deformed and cement particles remained on the surfaces of both the smooth glass and the cratered Surlyn(TM), but the plastic surface held many more particles than the glass surface.

Packages that had an aluminum foil vapor barrier and a polyethylene heat-sealable face performed well. The appearance of the Kraft paper substrates were slightly affected by the fog room exposures although the contents were preserved. The plastic substrates (Packages 4 and 6) gave the best external appearance after all tests. These plastic films (Mylar(TM) and Tyvek(TM)) also provide superior strength and external abrasion resistance; however, the Kraft paper substrates may accept and retain a printed label better than the plastic.

The smoothness of the polyethylene inner surfaces allowed easy discharging of the samples, although some cement was difficult to remove from the seams. The rough surface of the Surlyn(TM) trapped some of the smaller particles, which could not be removed even with camel-hair brushes and swabbing. Coupled with the problem of the organic residue found in the cement, it is not recommended the Surlyn(TM) be used as a heat-sealable inner liner.

Conclusions and Recommendations

Flexible packages made of laminated barrier materials containing pinhole-free aluminum foil and having polyethylene film as the sealing material were found to protect hygroscopic cement from hydration and carbonation. However, several factors mitigate against the use of these packages for cement:

(1) Chemicals in or on the surfaces of the plastic films can contaminate the cement.
(2) Sealing the packages is critical and should be performed with an automated sealing machine, which requires considerable capital investment. Cements may also interfere with proper sealing.
(3) Cement sticks to the inner surfaces of the flexible packages. Thus not all of the sample can be removed from its container and some segregation may occur.
(4) Manufacturers of the packaging films generally agree that the films will retain their initial properties for several years, but they will not guarantee them for as long as ten years.
(5) It is concluded that at this time flexible packages are not reliable for cement SRMs that may be in storage for ten or more years before use.