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Metals Analyses of Portland and Blended Cement Via Microwave Digester and Inductively Coupled Plasma Technologies

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ABSTRACT

The method involves a sample preparation technique through microwave digestion to extract eight metals (Si, Al, Mg, Ca, Fe, Na, K, and Ti) in Portland (SRM 1888b) and Blended (SRM 1881a) cement traceable to NIST, followed by spectrometric detection and quantitation via the simultaneous system inductively coupled plasma-optical emission spectroscopy (ICP-OES). A 0.2-gram sample of the materials was prepared for closed-system digestion at 1200W. After digestion, solutions were diluted in 50-mL dedicated polypropylene laboratory ware (volumetric flasks) and analyzed. Accordingly, the dilution and calibration patterns were determined. The analyses were performed in five replicates. The detections of Si, Al, Mg, Ca, Fe, K, and Ti following radial mode and Na via axial torch orientation gave satisfactory results. Reproducibility studies were conducted, and ICP-OES configurations were established for each element. The method was developed based on its figures of merit. The procedure was validated with exceptional performance, except that it was not robust at a higher sample mass. Operational maintenance procedures were established when many samples were run. Measurement uncertainty estimation is recommended to identify the sources and effects of measurement errors.

Introduction

Cement is made by heating a mixture of materials such as chalk or marl, shells, limestone, clay, shale, blast furnace slag, slate, iron ore, and silica sand. The resulting product is a fine powder composed mainly of oxides of silicon, calcium, magnesium, iron, and aluminum, along with small amounts of other elements such as potassium and sodium. Cement is valuable because it acts as a binding agent. When mixed with rocks or gravel and combined with water, the mixture hardens into concrete. During hydration, compounds like SiO_2, CaO, Fe_2O_3, and Al_2O_3 react to form aluminoferrite hydrates and calcium aluminosilicates, which are responsible for cement's hardening. Two reference materials were used in this validation study: one, the Portland (SRM 1888b), and one, the Blended (SRM 1881a), which is a Portland cement blended with slag and fly ash, which, when combined, improves the workability of plastic concrete and the strength and durability of hardened concrete. With such a combination, cost savings and strength increases are achieved.

The performance of cement depends on both its mineral and exact chemical composition. For instance, elevated MgO levels can lead to weakness in hardened cement [1]. The characteristics of the raw materials used in cement production can lead to significant variations in the finished product's chemical composition. As a result, chemical analysis of cement is

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essential for evaluating its quality and determining the specific applications for which a particular cement type is most suitable. Cement testing plays a vital role in ensuring product quality, assessing performance, maintaining quality control, meeting regulatory standards, and promoting cost-effective construction practices. Proper testing helps ensure that concrete structures are safe, durable, and compliant with required quality standards.

Chemical analysis is routinely applied in cement manufacturing for quality control, evaluation of quarry materials, and assessment of intermediate products. Professionals in construction and manufacturing may also analyze cement to confirm its suitability for intended applications and to avoid costly repairs or failures in the future.

Elemental analysis of cement can be used to estimate the proportion of each element present in a sample. Although mineral composition is often more critical in determining cement properties and quality, it is generally more difficult to measure directly.

Compared with mineral analysis, elemental analysis is easier to perform, and the resulting elemental ratios can be converted into weight fractions of the corresponding oxides in the sample. From these oxide ratios, the mineral composition of cement can then be estimated.

A wide range of techniques is available for elemental analysis, including atomic spectroscopy, gravimetric methods, X-ray photoelectron spectroscopy, and inductively coupled plasma (ICP) systems [2, 3]. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) instruments can be configured as radial or axial views. In the radial configuration, the plasma is viewed from the side, whereas in the axial configuration, it is viewed end-on (along its length). An axially viewed plasma is used for analysis, typically for samples that require high sensitivity. The limitations are low matrix tolerance and a limited dynamic range, resulting from physical effects and the configuration of the plasma torch and interface. For high matrix tolerance, a radially viewed plasma is used in this configuration, reducing sensitivity but improving matrix tolerance and dynamic range. And so, in the case of cement samples, these two modes were tested to assess the sensitivity of elemental components present. However, since extraction or sample preparation is considered the soul of any experiment, the performance capability during microwave digestion was substantial.

All developed analytical methods need to be validated to ensure that each measurement of the analyte content in the sample during routine analysis is close to the true value [4]. The method was developed based on its reliability characteristics. These include precision, accuracy, sensitivity, linear dynamic range, detection limit, selectivity, and ruggedness and robustness.

Experimental

Standard and Sample Preparations

Materials and reagents used include pure metal standards (Si, Al, Mg, Ca, Fe, Na, K, Ti) purchased from Merck Millipore. Deionized water, concentrated HNO_3, concentrated HCI, concentrated HF, and concentrated H_2SO_4 were prepared for the digestion of samples. The certified reference materials (CRMs) were SRM 1888b Portland Cement and Blended (SRM 1881a) traceable to NIST. The Anton Paar Multiwave 5000 microwave digester and Shimadzu ICPE-9800 Inductively Coupled Plasma systems were exploited by running replicated samples. Preparation for digestion at 1200W power of both Portland and Blended SRM was made by weighing 200.0 ± 0.1 mg of previously homogenized cement directly into the liners (TFM vessels) of the microwave digester (Table 1). Actual weights were recorded for recovery calculations. Six milliliters of concentrated HNO_3, two milliliters of concentrated HCl, and 0.5 milliliters of HF were added to each liner. Samples were allowed to stand for several minutes, with occasional swirling to release gases, until the reaction subsided. Each vessel was sealed with a vent closed, following the recommended digestion program.

Table 1. Microwave program

Step	Time	Temperature	Microwave power
1	10 minutes	220 °C	Up to 1200 W
2	20 minutes	220 °C	Up to 1200 W

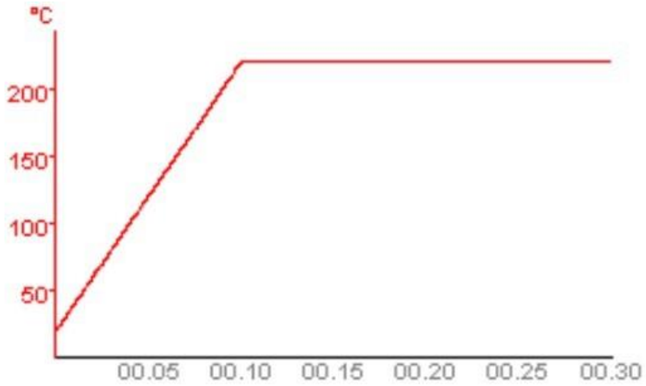


Fig. 1. Temperature profile during sample digestion

Fig. 1 shows the temperature profile of digestion. As shown, a 10-minute come-up time was set for the temperature to reach 220°C during heating. A ramping rate of about 19.5 °C/min takes place before digestion at a constant temperature for another 20 minutes. These conditions were achieved using a 1200-watt power supply.

When running more than eight vessels, 1200W power was used, and a balance inside the cavity was observed. After digesting and cooling, the venting nozzle was opened to release some pressure. Digestates were transferred quantitatively into plastic polypropylene 50mL volumetric flasks and made to volume with deionized water (solution A). A dilution pattern was followed accordingly (Table 2).

Table 2. Dilution pattern (Portland and blended cement)

Elements	Steps	Dilution rate
Ca, Mg, Al	as is (solution A)	50
Si, Fe, Na, K, Ti	Take 5 ml from solution A and dilute to 50 ml	500

Preparation of working standards involved using stock solutions of pure metals. Using the calibration pattern below, the volumes of stock solutions required to prepare a multi-element mixed standard solution were calculated. A calibrated digital pipettor was used for this preparation to ensure precise, accurate results and the linearity of the curves.

Table 3. Calibration range

Elements	Concentration (ppm)		
	I	II	III
Ca	50.0	100.0	200.0
Mg	2.5	5.0	10.0
Si	10.0	20.0	40.0
AI	2.5	5.0	10.0
K	25.0	50.0	100.0
Fe	25.0	50.0	100.0
Na	5.0	10.0	20.0
Ti	5.0	10.0	20.0

Quantification with ICP-OES

To operate the ICP, a sequence of steps was conscientiously followed, noting that what comes first during the turning on comes last during the shutting off. First, the breaker was switched on, then the cooling system, to ensure the pump was working. Then, the ICP system was turned on, providing a waiting time of at least 4 hours to achieve enough vacuum. The software was opened, and the "Analysis" button was clicked. After that, the argon supply was turned on to ensure the flow rate was properly set. Then, the appropriate method was downloaded, after which the plasma was turned on until all necessary initialization settings were made. Next, the wavelength calibration and registration of all samples and standard information were completed just before the analysis started. After the run, all necessary data and method information were saved, and data processing and evaluation followed. For data processing, the post-run (not real-time) was opened. Selected calibration data files were opened and evaluated to generate calibration curves. Once ready, the processing and integration of samples were completed.

A simple method for microwave-assisted preparation of cement reference samples is shown below (Fig. 2).

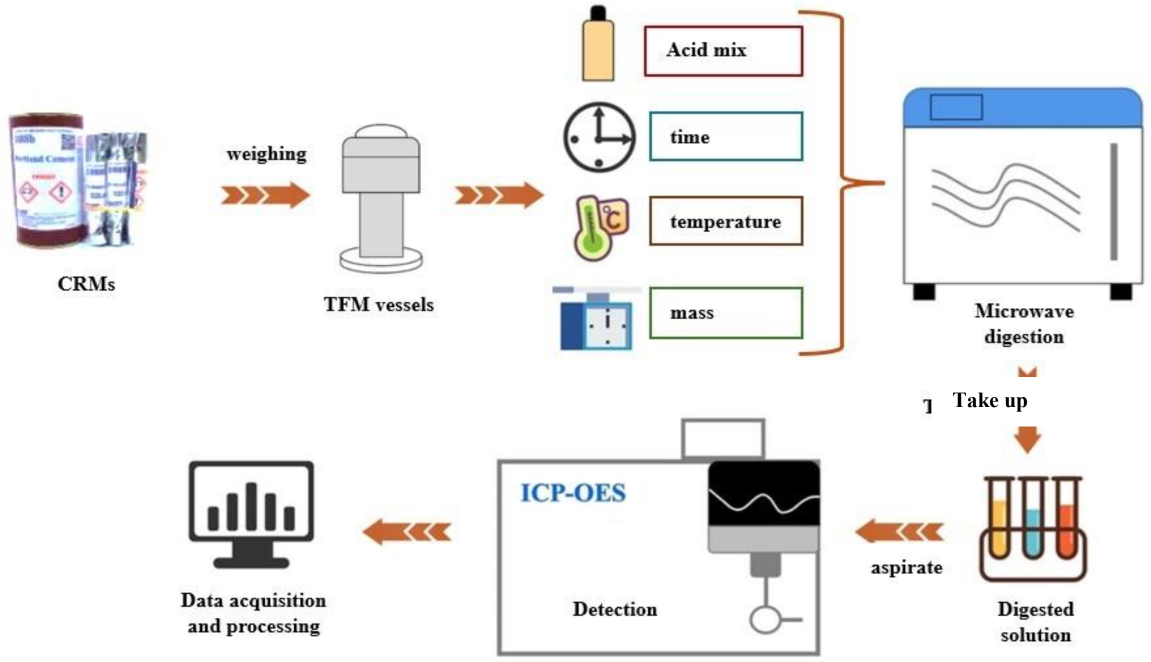


Fig. 2. The microwave-assisted preparation and ICP-OES digestion of cement samples

Wavelength Selection

Each element has a unique spectrum because it possesses a distinct number of protons and a specific arrangement of electrons. These spectral differences arise from variations in the energy absorbed or emitted by atoms when their electrons transition between different energy levels [5]. ICP-OES is an emission spectrophotometric technique in which excited electrons release energy at specific wavelengths as they return to their ground state. A key feature of this process is that each element emits radiation at characteristic wavelengths unique to its chemical identity [6]. However, when the excited electron returns to the ground state, it can take multiple pathways, each corresponding to the emission of a photon of a specific energy. Thus, a single absorption can lead to multiple emissions; consequently, more emission lines are observed in the atomic spectra of most elements. Although each element can emit energy at multiple wavelengths, ICP-OES typically focuses on one or only a few selected wavelengths for each element [7]. This approach enhances selectivity in detection. The intensity of the emitted radiation at the chosen wavelength is directly proportional to the concentration of the element in the sample. This can be seen in the generated calibration curves, where linearity and dynamic range are measured. ICP sensitivity is in the low parts-per-billion range [8]. The system uses a large-scale CCD (charged-coupled device) with an array of pixels, each sensitive to a specific wavelength, thereby enhancing the capture of photons emitted after absorption or during relaxation. That means that the entire chip, which is photoreactive, enables ICP to detect the various emission lines with great accuracy and sensitivity.

Reliability Characteristics

A comparison of the amount found with the target declaration on the certificates provides a measure of the method's recovery, which is an estimate of the technique's accuracy [9]. After the detection and quantification of the elements of interest, gravimetric conversion factors were used to convert each element to its stoichiometric oxide form as a component of cement (Table 4). Since the validation was carried out using the CRMs, accuracy was determined by comparing the measured concentrations with the certified values and expressed as percentage recovery (R%). This represents the "trueness" or the closeness of the analytical result to the "true" value. The smaller the recovery percentage, the greater the method's bias and thus its lower trueness. This measures how the technique can be improved and optimized, from sampling and preparation to detection. The acceptable recovery percentage depends on the analyte concentration. The acceptability criteria for recovery vary with concentration. The lower the concentration, the lower the probability of obtaining 100% of the element of interest, and the greater the likelihood of physical and chemical losses (Table 5).

Table 4. Conversion factors of each element to its stoichiometric oxide

Element	Stoichiometric oxides	Ratio	Conversion factor
Fe	Fe_2O_3	Fe_2O_3/Fe	1.4297
K	K_2O	K_2O/K	1.2046
Ti	TiO_2	TiO_2/Ti	1.6681
Na	Na_2O	Na_2O/Na	1.3480
Ca	CaO	CaO/Ca	1.3992
Mg	MgO	MgO/Mg	1.6582
Si	SiO_2	SiO_2/Si	2.1392
Al	Al_2O_3	Al_2O_3/Al	1.8895

In terms of precision, only reproducibility precision was evaluated. Repeatability precision is the agreement of results from at least seven replicates under common conditions, from extraction to aspiration in the ICP, to assess the routine performance of the method. However, repeatability precision was not evaluated. The normalized intensities of the specific element were among the bases for selecting the optimal detection wavelength. While the standard deviation of analytical data may remain relatively constant over a narrow range, it generally depends on the magnitude of the values. That is, larger measurements tend to produce larger standard deviations. Therefore, when comparing variability among such data (e.g., assessing precision), it is often more practical to use the relative standard deviation (RSD) rather than the absolute standard deviation. The RSD can be expressed as a fraction, but it is more commonly reported as a percentage, known as the coefficient of variation (CV or %RSD). The usual range for %RSD in analytical testing is 5–20%. Conversely, the reproducibility precision evaluates the closeness of results from several determinations done under varied conditions [10]. The dataset will explain the method's performance over a given period. This could be based on consensus values among laboratories performing the tests. The proficiency test using the CRMs can provide consensus values and thus be used to evaluate reproducibility precision. Reproducibility precision for each element was determined from the mean concentration values obtained from data generated under different conditions. The concentration of the analyte, C, was expressed as a mass fraction, where the numerator and denominator are in the same mass units, after which the $HorRat_R$ from the RSD_R was evaluated [11]. The predicted reproducibility relative standard deviation calculated from the Horwitz formula:

$$PRSD_R = 2C^{-0.15} \tag{1}$$

Acceptable reproducibility values typically range from 1/2 to 2 times the calculated value. Alternatively, a ratio can be calculated between the found value for RSDR and the value calculated from the HorRatR formula. Acceptable values for this ratio are typically 0.5 to 2.

$$HorRat_R = RSD_R\ (found,\ \%)\ /\ PRSD_R\ (calculated,\ \%) \tag{2}$$

This equation transformed the RSD found to a fraction of the RSD expected from applying the exponential equation to the concentration. The precision found was expressed as a fraction of the precision calculated from the experimental concentration estimates. It equals 1 for exact correspondence. The precision is better than expected when the ratio is less than 1 and poorer when it is greater than 1 [10]. Table 5 shows the recommended precision limits for accuracy and reproducibility as a function of concentration [12].

Table 5. Acceptable recovery and predicted relative standard deviations criteria

Concentration	**Recovery (%)**	**Reproducibility RSD_R, (%)**
100%	98-101	2
10%	95-102	3
1%	92-105	4
0.1%	90-108	6
0.01%	85-110	8
10 µg/g (10 ppm)	80-115	11
1 µg/g (1 ppm)	75-120	16
10 ng/g(10 ppb)	70-125	32

Note: AOAC Guidelines for Single-Laboratory Validation of Chemical Methods for Dietary Supplements and Botanicals (2012) Official Methods of Analysis, 19th Ed., Appendix K, AOAC INTERNATIONAL, Gaithersburg, MD

The linear dynamic range refers to the range of concentrations an instrument can measure, from the minimum to the maximum detectable (Fig. 3). The range provides satisfactory reliability, as indicated by Coefficient of Determination (R^2) values, as explained in the next criterion, linearity. The linearity of the curve can be used to assess reliability. Calibration curves must show a correlation coefficient (R) of at least 0.999 [13]. In other words, R^2 indicates how well the data fit the regression model (the goodness-of-fit).

The limit of detection (LOD) was estimated from the residual standard deviation (s_r) of a calibration curve, which measures the scatter of the data points around the regression line [14]. The STEYX function in Microsoft Excel directly calculates the residual standard deviation, also known as the standard error of the estimate. It requires the input ranges for the y and x values. For LOD, the formula is:

$$LOD = 3.3 \times s_r/S \tag{3}$$

where s_r is the residual standard deviation, and S is the slope of the calibration curve.

This method uses linear regression of your calibration data to estimate the slope and residual standard deviation. To calculate the limit of quantification (LOQ), the formula below was used.

$$LOQ = 10 \times s_r/S \quad (4)$$

Figures of merit are described in Fig. 3.

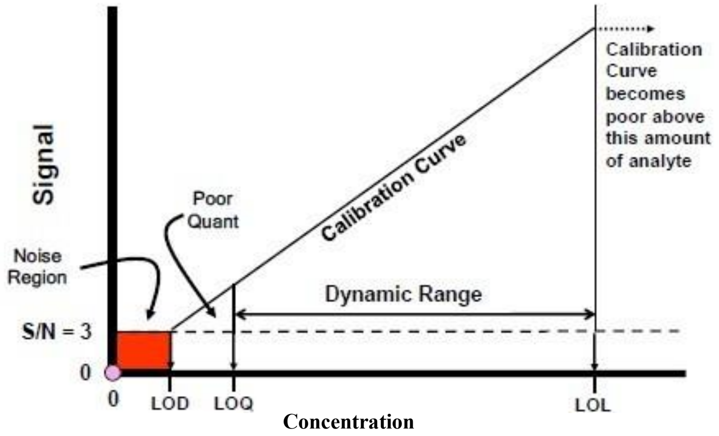


Fig. 3. Calibration curve, and figures of merit [13]

The robustness, or ruggedness, of an analytical method refers to its ability to remain unaffected by small, deliberate variations in experimental conditions, indicating the method's reliability under normal operating conditions [15]. A ruggedness test is a part of method validation and can be considered part of the precision evaluation. Ruggedness is related to repeatability and reproducibility [16]. Robustness is the method's ability to resist change without adapting its initial stable configuration. Ruggedness is a measure of the reproducibility of test results under variations in conditions other than the laboratory.

Results and Discussion

Selectivity and Sensitivity

The selection of wavelengths was based on the normalized intensities for each element obtained for this type of matrix, namely, cement. This objective was established by running several replicates of the reference materials under the same and varied conditions using the standard radial mode and assessing which elements needed to be introduced axially (Table 6). Some elements were evaluated using more than one reference wavelength at which energy emission intensities are high and optimum. These are the results when the excited electron returns to the ground state. It can take multiple pathways, each corresponding to the emission of a photon of a specific energy. Thus, a single absorption can lead to multiple emissions; consequently, more emission lines at different wavelengths are observed in atomic spectra. These multiwavelength elements are the Ca (183.801, 220.861, and 616.217), Fe (235.489, 239.562), K (766.490, 769.896), and Na (330.232, 588.995, 589.592). After selecting the optimal emission wavelength, the actual calibration curves were assessed. Parameters included high and normalized intensities, goodness-of-fit (R^2), and standard intensities, all of which were proportional to corresponding concentrations.

All the elements (Ca, Mg, Si, Al, Fe, K, Na, and Ti) show comparable responses except for Na. Na reflects low intensities (denoted by the letter "L"), which vary appreciably from one to another. This suggests that Na would give optimal emission intensities if 100% of the sample were nebulized into the plasma via the axial mode. Table 7 summarizes the corresponding selective wavelengths and sensitive plasma viewing orientation for analyzing each element of interest.

Table 6. Recorded intensities for Ca, Mg, Si, Al, Fe, K, Na, and Ti

Sample Name	**Al 396.153**	**Ca 183.801**	**Ca 220.861**	**Ca 616.217**	**Fe 235.489**	**Fe 239.562**	**K 766.490**	**K 769.896**	**Mg 280.270**	**Na 330.232**	**Na 588.995**	**Na 589.592**	**Si 288.158**	**Ti 336.121**
Portland 1	12100	371000	323000	414000	26500	22100	5310	5540	!!!!!!!	2760 L	181	231	107000	1270
Portland 2	14300	375000	323000	418000	26700	21100	5310	5520	!!!!!!!	2780 L	184	234	112000	1260
Portland 3	14700	378000	321000	413000	26500	21300	5270	5530	!!!!!!!	2840 L	187	235	106000	1250
Portland 4	14800	377000	323000	414000	26400	21200	5250	5530	!!!!!!!	2820 L	179	227	109000	1250
Portland 5	14700	376000	324000	411000	26400	21500	5270	5540	!!!!!!!	2840 L	182	231	109000	1250
Portland 6	15600	379000	323000	420000	26600	21200	5290	5540	!!!!!!!	2840 L	181	230	108000	1260
Portland 7	15300	377000	321000	415000	26500	21000	5270	5520	!!!!!!!	2830 L	180	229	112000	1250
Mean Average	14500	376143	322571	415000	26514	21343	5281	5531	#DIV/0!	#DIV/0!	182	231	109000	1256
Standard Dev.	1142	2610	1134	3055	107	369	23	9	#DIV/0!	#DIV/0!	3	3	2309	8
%RSD	7.873	0.694	0.352	0.736	0.403	1.729	0.429	0.163	#DIV/0!	#DIV/0!	1.488	1.199	2.119	0.627
Portland 8	16100	337000	294000	364000	25800	21900	10300	10600	!!!!!!!	2850 L	251	303	119000	1990
Portland 9	20200	346000	291000	373000	25800	21100	10300	10500	!!!!!!!	2840 L	254	305	121000	2000
Portland 10	17900	337000	291000	367000	25700	21500	10300	10500	!!!!!!!	2840 L	253	306	118000	1990
Portland 11	19500	335000	293000	367000	25600	21400	10300	10500	!!!!!!!	2830 L	254	307	118000	1980
Portland 12	23300	345000	297000	374000	25700	21500	10300	10600	!!!!!!!	2830 L	250	303	116000	1990
Portland 13	20000	348000	290000	376000	25900	21200	10300	10500	!!!!!!!	2810 L	258	309	120000	2010
Portland 14	21000	343000	292000	371000	25600	21500	10200	10500	!!!!!!!	2820 L	249	301	112000	1990
Mean Average	19714	341571	292571	370286	25729	21443	10286	10529	#DIV/0!	#DIV/0!	253	305	117714	1993
Standard Dev.	2281	5159	2370	4386	111	257	38	49	#DIV/0!	#DIV/0!	3	3	2984	10
%RSD	11.572	1.510	0.810	1.185	0.432	1.200	0.367	0.463	#DIV/0!	#DIV/0!	1.203	0.897	2.535	0.477
Portland 15	15400 L	467000	403000	447000	32100	24800	5290	4450	22100	6300 L	271	521	137000	1240
Portland 16	18000	473000	401000	454000	32100	24400	5220	4280	22200	6190 L	245	497	124000	1240
Portland 17	18600	468000	399000	450000	32000	24700	4540	3470	22100	5920 L	166	422	115000	1230
Portland 18	18600	471000	405000	449000	31800	24700	5130	4040	22100	6050 L	311	569	113000	1220
Portland 19	18600	474000	399000	457000	32100	24700	5210	3780	22300	5650 L	293	563	115000	1240
Portland 20	19500	479000	400000	457000	32000	24500	5200	3820	22200	5590 L	262	530	109000	1240
Portland 21	19100	471000	399000	451000	31700	24700	4660	3380	22000	5520 L	159	425	107000	1230
Mean Average	18257	471857	400857	452143	31971	24643	5036	3889	22143	#DIV/0!	244	504	117143	1234
Standard Dev.	1344	4018	2340	3934	160	140	303	396	98	#DIV/0!	60	60	10303	8
%RSD	7.361	0.851	0.584	0.870	0.502	0.567	6.022	10.188	0.441	#DIV/0!	24.406	11.932	8.795	0.637
Blended 1	19900 L	419000	357000	403000	30300	24500	9500	7910	18400	4610 L	83.7	351	113000	2090
Blended 2	24300	432000	362000	407000	30200	24300	9840	8460	18500	4960 L	188	449	109000	2070
Blended 3	21900	426000	359000	402000	30100	24400	9910	8450	18400	4880 L	205	466	110000	2070
Blended 4	23700	425000	358000	402000	30000	24300	10300	8760	18400	4800 L	302	560	110000	2060
Blended 5	27800	436000	360000	413000	30200	24300	9570	7880	18700	4640 L	119	388	109000	2090
Blended 6	24000	428000	352000	405000	30000	24000	9650	8160	18500	4610 L	156	418	111000	2070
Blended 7	25400	422000	363000	404000	30100	24400	10000	8570	18400	4710 L	213	472	105000	2060
Mean Average	23857	426857	358714	405143	30129	24314	9824	8313	18471	#DIV/0!	181	443	109571	2073
Standard Dev.	2505	5786	3638	3891	111	157	278	337	111	#DIV/0!	71	67	2440	13
%RSD	10.501	1.355	1.014	0.960	0.369	0.647	2.834	4.048	0.602	#DIV/0!	39.223	15.186	2.227	0.605
Blended 8	15000	314000	274000	339000	24000	20400	9640	9880		2650 L	233	283	111000	1860
Blended 9	18600	319000	269000	344000	23800	19500	9500	9720	!!!!!!!	2620 L	234	282	111000	1850
Blended 10	16500	310000	268000	339000	23700	19800	9460	9690	!!!!!!!	2610 L	233	282	109000	1840
Blended 11	18100	310000	272000	341000	23800	19800	9510	9730	!!!!!!!	2630 L	236	285	110000	1840
Blended 12	21700	322000	277000	349000	24000	20000	9620	9860	!!!!!!!	2640 L	233	282	108000	1860
Blended 13	18500	323000	269000	348000	24000	19700	9550	9760	!!!!!!!	2610 L	239	287	111000	1870
Blended 14	19600	319000	272000	345000	23900	20000	9510	9760	!!!!!!!	2630 L	232	280	105000	1850
Mean Average	18286	316714	271571	343571	23886	19886	9541	9771	#DIV/0!	#DIV/0!	234	283	109286	1853
Standard Dev.	2143	5407	3207	4077	121	285	66	72	#DIV/0!	#DIV/0!	2	2	2215	11
%RSD	11.718	1.707	1.181	1.187	0.509	1.435	0.694	0.734	#DIV/0!	#DIV/0!	1.037	0.816	2.026	0.601
Blended 15	18600 L	391000	333000	376000	28300	22800	8850	7370	17100	4290 L	78	327	105000	1950
Blended 16	22500	398000	334000	376000	27900	22400	9080	7800	17100	4580 L	173	415	101000	1910
Blended 17	20200	392000	331000	371000	27800	22400	9130	7780	16900	4490 L	189	430	101000	1910
Blended 18	22000	395000	332000	373000	27900	22500	9520	8120	17100	4450 L	280	520	102000	1910
Blended 19	26000	406000	336000	385000	28200	22600	8930	7350	17500	4330 L	111	362	101000	1950
Blended 20	22200	397000	326000	376000	27800	22300	8960	7570	17100	4270 L	144	388	103000	1920

Blended 21	23600	393000	338000	377000	28000	22800	9310	7980	17200	4380 L	199	439	98200	1920
Mean Average	22157	396000	332857	376286	27986	22543	9111	7710	17143	#DIV/0!	168	412	101600	1924
Standard Dev.	2362	5099	3848	4386	195	199	235	294	181	#DIV/0!	66	62	2094	18
%RSD	10.661	1.288	1.156	1.166	0.697	0.882	2.581	3.814	1.057	#DIV/0!	39.171	15.052	2.061	0.942

Note: Samples were aspirated using the default sample introduction mode, with the nebulizer radial to the torch, which served as the plasma source.

Table 7. Specific wavelength and introduction mode for each element

Elements	**Ca**	**Mg**	**Al**	**Si**	**Fe**	**K**	**Ti**	**Na**
λ (nm)	183.801	280.27	396.153	288.158	239.562	769.896	336.121	330.232
Mode	radial	radial	Radial	radial	radial	radial	radial	axial

Accuracy and Precision

The oxide constituents of the Portland-type cement samples were computed, as shown in Table 4. Five replicate runs were made at different conditions (Table 8). The average values were calculated and were presented as the mean ± standard deviation of these trials. Plotting these results would show the comparison between average percentage recoveries from five replicate runs at different conditions and the target concentrations. These graphs (Figs. 4 & 5) display the profile of the cement types in terms of their stoichiometric oxides.

Table 8. Summary of concentrations of oxide constituents replicated at different conditions and corresponding percentage recovery (R)

Oxide Components	**Mode**	**Target, %**		**Actual, %**										**Average, %**		**Recovery (R), %**	
		Portland	**Blended**	**Portland**					**Blended**					**Portland**	**Blended**	**Portland**	**Blended**
				1st	**2nd**	**3rd**	**4th**	**5th**	**1st**	**2nd**	**3rd**	**4th**	**5th**				
CaO	Radial	63.13 ± 0.29	57.58 ± 0.34	62.64	64.22	63.02	64.52	63.26	57.19	57.23	55.55	54.87	56.69	63.53 ± 0.80	56.31 ± 1.05	100.6	97.8
MgO		3.562 ± 0.057	2.981 ± 0.077	3.27	3.38	3.31	3.45	3.67	2.79	2.78	2.73	2.79	3.06	3.42 ± 0.16	2.83 ± 0.13	95.9	95.0
Al_2O_3		4.277 ± 0.036	7.06 ± 0.081	4.02	3.52	3.96	4.30	4.48	6.23	6.19	6.77	6.56	6.73	4.06 ± 0.37	6.50 ± 0.27	94.9	93.1
SiO_2		20.42 ± 0.23	22.26 ± 0.15	20.10	20.23	20.27	20.30	20.52	22.15	23.16	22.22	22.51	22.38	20.28 ± 0.15	22.48 ± 0.40	99.3	101.0
Fe_2O_3		3.062 ± 0.053	3.09 ± 0.11	3.12	3.07	3.07	3.02	3.05	3.28	3.10	3.07	3.03	3.07	3.07 ± 0.04	3.11 ± 0.10	100.1	100.6
K_2O		0.658 ± 0.017	1.228 ± 0.029	0.63	0.64	0.60	0.60	0.67	1.22	1.22	1.15	1.15	1.27	0.63 ± 0.03	1.20 ± 0.05	94.8	98.1
TiO_2		0.2316 ± 0.0076	0.3663 ± 0.0030	0.20	0.20	0.22	0.19	0.21	0.33	0.33	0.32	0.33	0.33	0.20 ± 0.01	0.33 ± 0.004	91.4	89.8
Na_2O	Axial	0.1364 ± 0.0044	0.199 ± 0.007	0.12	0.13	0.10	0.09	0.16	0.19	0.13	0.18	0.13	0.25	0.12 ± 0.03	0.18 ± 0.05	91.3	90.7

Note: The average recoveries are reported as mean ± standard deviation of the five reproducible replicates. Oxides of Ca, Mg, Al, Si, Fe, K, and Ti have achieved acceptable radial recovery values. The axial mode of sample introduction on Na gave satisfactory recoveries for both cement types.

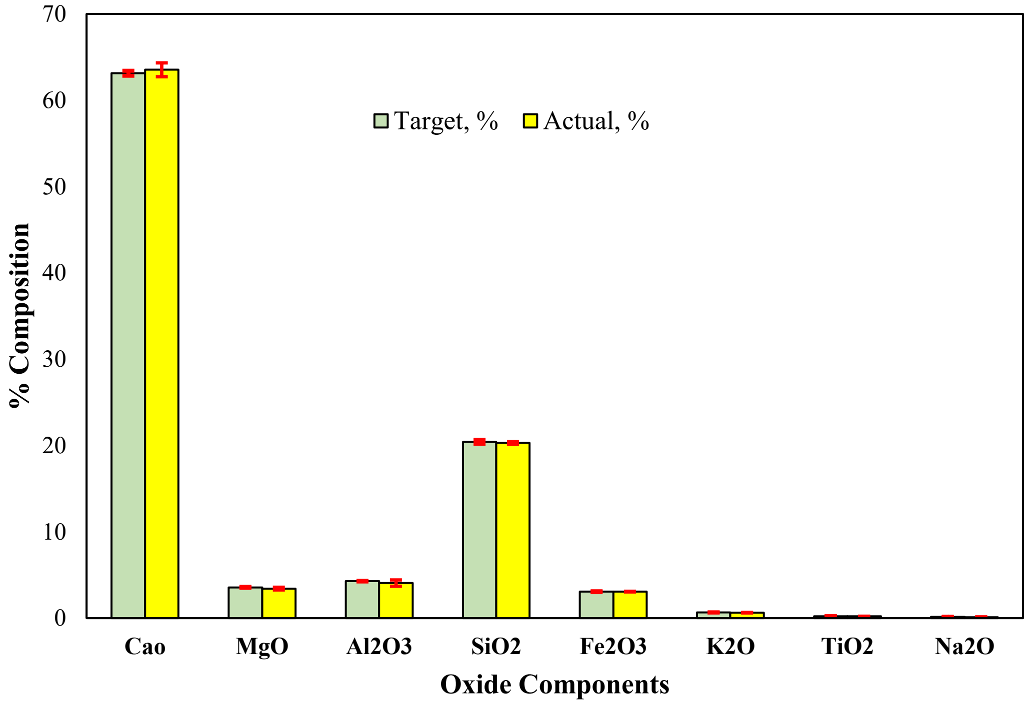


Fig. 4. Oxide constituents' profile of the Portland cement (SRM 1888b)

For the Blended type (SRM 1881a), Fig. 5 shows the cement profile and the comparable target and actual percentages, along with predefined and calculated standard deviations.

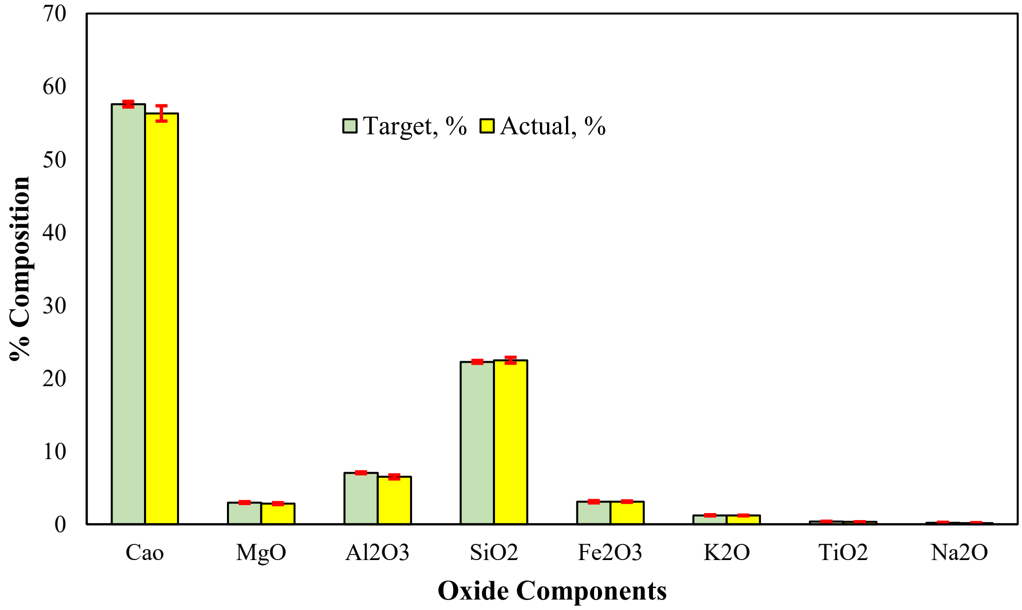


Fig. 5. Oxide constituents' profile of the Blended (SRM 188la) cement

All components, except Na_2O, have achieved acceptable recovery values at the radial mode of sample introduction. In the case of Na_2O, the axial mode of sample introduction also yielded satisfactory recoveries relative to the targets, confirming the high accuracy and precision of the closed-system microwave acid digestion and ICP-OES detection.

It can be observed that the corresponding standard deviation values of each component from both cement types were higher than the standard values. This implies that all the uncertainties attributable to the developed method must be established. The estimation uses calibration certificates for all paraphernalia involved in the analysis and accounts for the factors affecting uncertainty. With this, every effort is made to optimize the measurement procedure. However, the measurement result can only serve as an estimate of the true value, which is inherently unknown. As a result, the closeness of the measured value to the true value cannot be precisely determined, and every measurement carries some degree of uncertainty. The quality and accuracy of a measurement are described by its measurement uncertainty, which defines a range around the measured value within which the true value is expected to lie with a certain probability.

Reproducibility Precision

The set of five reproducibility data was evaluated through their HorRat$_R$ values. Concentrations were expressed as a decimal fraction. For reporting HorRat$_R$ values, data were reported as mass fractions, with the numerator and denominator units the same (Table 9).

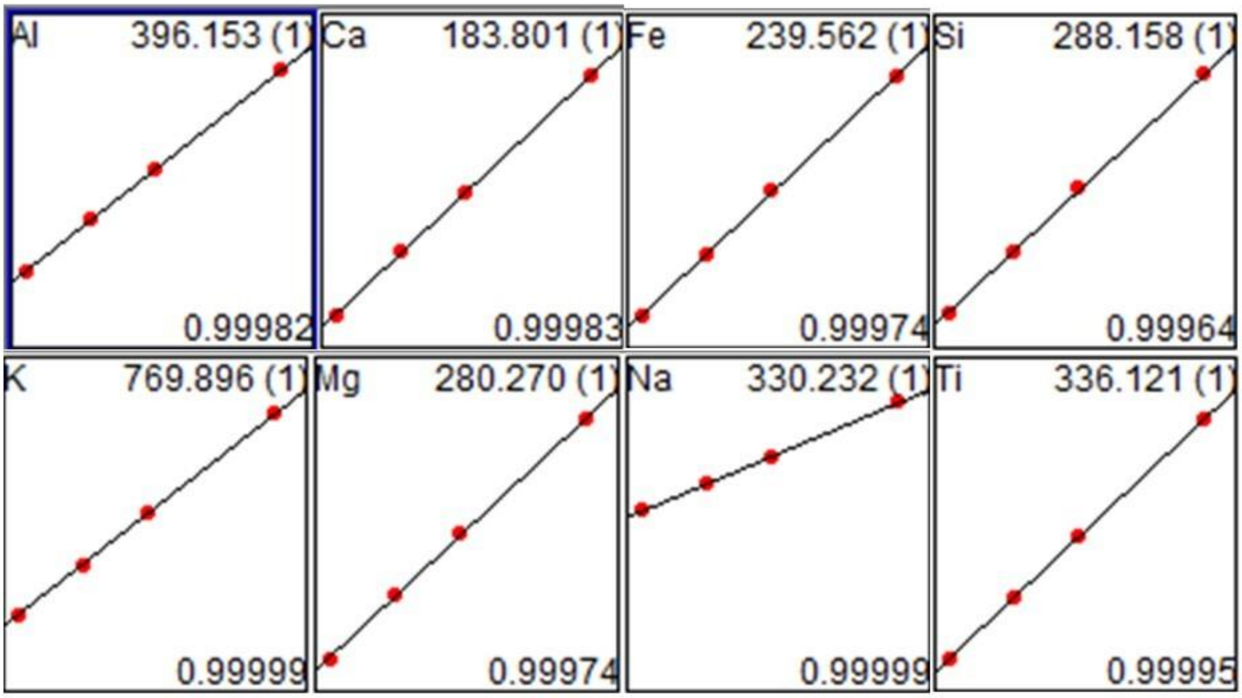
Table 9. Reproducibility precision factors

Constituents	Mass fraction		RSD$_R$		PRSD$_R$		HorRat$_R$	
			Portland	**Blended**	**Portland**	**Blended**	**Portland**	**Blended**
Cao	0.6353	0.5631	2.1408	2.1800	2.1429	2.1727	0.9991	1.0034
MgO	0.0342	0.0283	3.3189	3.4138	3.2982	3.3875	1.0063	1.0078
Al_2O_3	0.0406	0.0649	3.2344	3.0141	3.2089	2.9817	1.0079	1.0109
SiO_2	0.2028	0.2249	2.5407	2.5018	2.5382	2.5055	1.0010	0.9985
Fe_2O_3	0.0307	0.0311	3.3732	3.3662	3.3739	3.3693	0.9998	0.9991
K_2O	0.0062	0.0120	4.2831	3.8808	4.2491	3.8695	1.0080	1.0029
TiO_2	0.0020	0.0033	5.0625	4.7206	4.9945	4.6451	1.0136	1.0163
Na_2O	0.0012	0.0017	5.4810	5.1869	5.4068	5.1113	1.0137	1.0148

As expected, the predicted relative standard deviations, PRSD$_R$, are within 2 to 6 based on the criteria (Table 5). This also holds for the found RSD$_R$. Since the correspondence between actual and expected values is almost exact, the actual HorRatR values are likely close to 1.0, indicating that the method complies with AOAC criteria at high precision and that method reproducibility is acceptable.

Linearity

Standard calibration curves and linearity (goodness of fit) were evaluated based on R^2 (Fig. 6).



Note: These curves were extracted from the software during the validation run.

Fig. 6. Calibration curves using emission wavelengths of the element of interest

The R^2 shows how well a regression model, based on a series of standard concentrations for each element, predicts the outcome of the observed data, which is the element of interest in the sample.

In Shimadzu ICP software for ICP-OES, the general form of the calibration equation for a curve fit (often a linear or polynomial regression) in the software is:

$$C = aI^3 + bI^2 + cI + d \tag{5}$$

where C is the calculated concentration of the analyte in the sample, I is the measured signal intensity, and c is the slope (sensitivity) of the linear portion of the calibration curve, which represents the change in concentration per unit of intensity. d is the y-intercept (offset) of the calibration curve. Ideally, this value should be close to zero if the blank measurement is zero and forced through the origin, but it can deviate due to background signals or instrumental drift.

In a simple linear calibration (which is typical for most ICP analyses over a specific range), the a and b coefficients are typically set to zero, and the equation simplifies to the linear equation:

$$C = cI + d \tag{6}$$

where the values for c and d are coefficients in the equation used to calculate the concentration from the measured signal intensity [17], the linearity of the calibration curves was considered suitable for quantitation, with each having a correlation coefficient (R)> 0.999, yielding a correlation coefficient of determination (R^2)> 0.999 (Table 10).

Table 10. Slope-intercept form of the equation of a straight line

Element	WL	R	Order	Origin	*c*	*d*	R^2
Al	396.153	0.99982	1	None	0.0049289	-2.912801	0.99964
Ca	183.801	0.99988	1	None	0.2096049	-5.524775	0.99976
Fe	239.562	0.99974	1	None	0.1009963	-6.142189	0.99948
K	769.896	0.99974	1	None	0.0176263	-29.38522	0.99948
Mg	280.270	0.99982	1	None	4.654416e-04	-1.036646	0.99964
Na	330.232	0.99999	1	None	0.0401324	-29.76960	0.99998
Si	288.158	0.99964	1	None	0.0072147	-3.187411	0.99928
Ti	336.121	0.99995	1	None	2.568835e-04	-0.2780649	0.99990

Note: These values were extracted from the software during the validation study.

As observed, not all the lines pass through the origin. This means all the standard intensities have a non-proportional linear relationship with the standard concentrations. Furthermore, the medium used for standard preparation contains trace amounts of these elements, resulting in intrinsic response or matrix effects when running a blank.

Range

Samples with high analyte concentrations were diluted with suitable solvents to bring them within the prepared calibration range. The validation has established a dilution pattern (Table 2) to suit the concentration of the analytes present in SRM 1888b and SRM 1881a and fall within the calibration range (Table 3). The evaluation of the method's performance characteristics, particularly the accuracy, precision, and linearity, has validated the calibration patterns to be applicable for detecting and quantifying the elemental Al, Ca, Fe, K, Mg, Na, Si, and Ti, and their equivalent oxide forms when analyzing actual Portland and Blended commercial types of cement. The plasma sample introduction configuration was considered a critical part of this method validation study to establish optimal recoveries of these elements. The dilution step was crucial, given that the analysis would be performed simultaneously. However, the linear dynamic range of the ICP, in which the concentration range and the corresponding signals are directly proportional to the sample concentration, was not determined. This can be achieved by preparing a higher standard concentration for each analysis and assessing the goodness-of-fit of the line at the point where R^2 begins to decrease, taking into account the corresponding limit of detection (LOD) and limit of quantification (LOQ).

Limit of Detection (LOD)/Limit of Quantification (LOQ)

The limits of detection (LOD) and quantification (LOQ) were determined based on the calibration curve's linearity and its standard error. LOD is defined as the lowest concentration of an analyte that can be detected by the instrument and is not significant for linearity and precision testing. The LOQ is the lowest concentration at which the analyte can be reliably quantified at a 95% confidence interval. Given the calibration curve for each element, the x and y values, and the measured intensities, the residual standard deviation (s_r) for each curve was calculated using the STEYX function in Excel.

Table 11 shows the calculated residual standard deviation for each element with the corresponding LOD and LOQ.

Table 11. LOD and LOQ values

Elements	Residual Standard Deviation, s_r	Estimated limits (ppm)	
		LOD	LOQ
Ca	0.064	1.0	3.0
Mg	1.5×10^{-5}	0.1	0.3
Si	0.025	12.0	40.0
Al	0.0007	0.5	1.5
K	0.130	25.0	74.0
Fe	0.012	0.4	1.2
Na	0.05	4.1	12.5
Ti	5.4×10^{-5}	0.07	0.21

Sample calculations are shown as part of the supplemental information of this manuscript.

Ruggedness/Robustness

The ruggedness of the method was evaluated based on the reproducibility precision results. Under varying conditions, it was observed that the predicted relative standard deviations ($PRSD_R$) and the relative standard deviations (RSD_R) are within the criteria, resulting in actual $HorRat_R$ values approximately equal to 1.0, meaning the method is rugged.

The method's robustness was challenged by altering the sample size for digestion from 0.2 to 0.5 grams, while maintaining the volumes of the added reagents and detection settings. The objective was that the greater the sample size, the more representative the sample is, and the higher the recovery. However, after the microwave digestion of 0.5-gram samples, the oxides of Ca, Mg, Al, Ti, and Na did not exhibit satisfactory results with increasing sample size. It was noticeable that, at a 0.5-gram sample, Na recoveries were poor with the torch in the axial orientation. Therefore, the method has become less robust when analyzing larger sample sizes. This may be due to salt deposits or eventual clogging in the nebulizer [18, 19]. Digesting 0.5 grams of sample and bringing it to a specific volume before introduction into the ICP-OES has resulted in intensely colored digestates. Potential concentration gradient within the sample solutions could affect the ionization process, and varying flow rates or residence times of these solutions within the nebulizer. The likely presence of matrix effects influencing the analysis's sensitivity would therefore call for additional procedures such as standard addition, dilution, separation, filtration, etc., and some of these can significantly contribute to detection errors [20, 21]. These extra steps can introduce additional uncertainty and variation into the analysis, resulting in a larger bias. Table 12 shows the comparison in terms of test for method robustness between using 0.2- and 0.5-gram samples for analyzing CRMs.

Table 12. Test for robustness data

Component	**Mode**	**Targets, %**		**Actual, %**				**Recovery, %**				**NIST compliance**			
		Portland	**Blended**	**Portland**		**Blended**		**Portland**		**Blended**		**Portland**		**Blended**	
				0.2 g	0.5 g	0.2 g	0.5 g	0.2 g	0.5g	0.2 g	0.5 g	0.2 g	0.5 g	0.2 g	0.5 g
CaO	Radial	63.13 ± 0.29	57.58 ± 0.34	63.1	55.83	57.58	57.79	99.96	88.4	100.0	100.4	✓		✓	✓
MgO		3.562 ± 0.057	2.981 ± 0.077	3.3	----	2.8	2.7	93.6	----	94.6	90.7	✓		✓	✓
Al_2O_3		4.277 ± 0.036	7.06 ± 0.081	4.1	4.0	6.5	4.8	95.9	93.2	92.1	68.9	✓	✓	✓	
SiO_2		20.42 ± 0.23	22.26 ± 0.15	20.5	19.1	22.9	20.4	100.3	93.7	102.8	91.5	✓	✓	✓	✓
Fe_2O_3		3.062 ± 0.053	3.09 ± 0.11	3.06	2.82	3.23	3.13	99.9	92.1	104.5	101.3	✓	✓	✓	✓
K_2O		0.658 ± 0.017	1.228 ± 0.029	0.64	0.63	1.23	1.18	97.3	95.7	100	96.03	✓	✓	✓	✓
TiO_2		0.2316 ± 0.0076	0.3663 ± 0.0030	0.23	0.19	0.33	0.30	98.7	82.9	91.1	82.9	✓		✓	
Na_2O	Axial	0.1364 ± 0.0044	0.199 ± 0.007	0.13	0.11	0.18	0.17	93.8	80.7	91.0	85.4	✓		✓	

Note: Analysis of magnesium using 0.5-gram samples has exceeded the equipment's detection limit. Potential saturation during detection has occurred, indicating a need to optimize the response through dilution or a decrease in sample size. Other metals, such as Ca, Al, Ti, and Na, have reached the detection limit and thus affected the linear range. Consequently, this has resulted in slightly lower intensities, which have led to slightly lower concentrations. The (✓) indicates assay conformity of each component according to the NIST Certificates of Analysis for Portland (SRM 1888b) and Blended (SRM 1881a).

Conclusion

The findings of this study demonstrate that the developed analytical method is reliable and effective for both Portland and blended cement samples. With appropriate in-house validation using local reference materials, the protocol is also expected to apply to masonry-type samples. The method's performance was supported by acceptable figures of merit obtained from 0.2-gram samples digested in a closed-vessel microwave system and analyzed according to the established calibration protocol. Routine operations using microwave-ICP were successfully carried out with dedicated polypropylene or non-contaminating laboratory ware to minimize carryover of sodium, silicon, and aluminum. Optimal plasma viewing modes were identified, with axial mode required for sodium and radial torch alignment for aluminum, calcium, magnesium, potassium, silicon, titanium, and iron determinations.

Despite the overall success of the validation study, the method showed limitations when applied to larger (0.5-gram) samples, indicating a lack of robustness at higher sample masses. Future work should include establishing the instrument's linear dynamic range by verifying calibration performance (e.g., R^2 values) across a range of concentrations. Routine quality control measures such as periodic introduction of check samples or distilled water, regular inspection of the sample introduction system, and proper maintenance of pump tubing and rinse solutions are essential to ensuring analytical integrity. Finally, estimating measurement uncertainty is recommended to quantify potential sources of error better and strengthen confidence in the method's applicability for routine cement analysis.

Conflicts of Interest

The author declares that no conflicts of interest exist.

Nomenclature

C	Concentration of the analyte
HorRat_R	Horwitz ratio (HorRat) or a normalized performance parameter indicating the acceptability of the method of analysis with respect to reproducibility precision.
PRSD_R	Predicted reproducibility relative standard deviation (%)
RSD_R	Reproducibility relative standard deviation (%)
s_r	Residual standard deviation

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