Application Note

Stability Test on Ca in Cement

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1 Introduction

This Application Note describes the stability and reproducibility test on Ca in cement, including the optimized conditions for the test. The samples were prepared in lithium metaborate and an internal standard was used to enhance the accuracy and precision.

2 Principle

2.1 Technique used

The elemental analysis of these samples was undertaken by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). The sample is nebulized then transferred to an argon plasma. It is decomposed, atomized and ionized whereby the atoms and ions are excited. We measure the intensity of the light emitted when the atoms or ions return to lower levels of energy. Each element emits light at characteristic wavelengths and these lines can be used for quantitative analysis after a calibration.

2.2 Internal standard

Correction of intensities by using an internal standard is very important for the analysis of major elements if precision is important; it enables compensation of signal changes due to changes in plasma conditions, changes in sample matrices or variations in nebulization efficiency. To apply this correction the choice of the internal standard element is crucial. It should have the same behavior as the element to be correct. The line type of the analyte should be the same, that is, if the line is atomic then the internal standard line should also be atomic or if it is ionic, a corresponding ionic internal standard line should be used. Additionally, the transitional energies of the analyte and the internal standard should be similar. A rough guide to transitional energy is to choose similar wavelengths.

Several tests were made using different elements as an internal standard. For example, Y was used, but the short-term repeatability was not corrected well. Next, the 341.476 nm Ni line was employed as internal standard. This is an atomic line with an excitation energy of about 3 eV, which are similar properties to those of the 422.673 nm Ca line. So, we can assume a similar behavior between the two lines.

Two corrections were made:
1. A simultaneous correction (Ca sim)
2. A sequential correction (Ca seq)

The simultaneous correction is made using an additional monochromator, on which a portion of the incident light is sent. The measurement of Ca and Ni are done at the same time.

The sequential correction is done simply by adding to the method the Ni line. Version 5 of the JY software calculates the ratio from both intensities. Whereas, Version 4, this correction would need to be done manually.

3 Sample preparation

The sample was prepared with 2 g of lithium metaborate and 5 % HCl.

4. Instrument specification

The work was done on a JY ULTIMA instrument and is also applicable to the JY 2000 ICP spectrometer. The specifications of this instrument are listed in Tables 1 and 2.

Table 1: Specification of spectrometer

Parameters	Specifications
Mounting	Czerny Turner
Focal length	1m
Nitrogen purge	Yes
Variable resolution	Yes
Grating number of grooves	2400 gr/mm
Order	2nd order

Table 2: Specification of RF Generator

Parameters	Specifications
Type of generator	Solid state
Observation	Radial
Frequency	40.68 MHz
Control of gas flowrate	by computer
Control of pump flow	by computer
Cooling	air

5 Operating conditions

The operating conditions are listed in Table 3 below.

Table 3: Operating conditions

Parameter	Condition
RF Generator power	1200 W
Plasma gas flowrate	14 L/min
Auxiliary gas flowrate	0 L/min
Sheath gas flowrate	0.35 L/min
Nebulizer flowrate	2 bars (29 psi)
Sample uptake	1 mL/min
Type of nebulizer	Concentric K3
Type of spray chamber	Scott
Argon humidifier	Yes
Injector tube diameter	3.0 mm

The K3 nebulizer is specifically dedicated to high salt content matrices. In the case of lithium metaborate, it is used with an argon humidifier. To obtain good short and long term stabilities a Scott spray chamber was chosen, which sorts the aerosol droplets more efficiently. The sheath gas flowrate was increased to avoid salt deposit on the injector tube. An AS 421 autosampler was used for the analysis. An 120 s was used as a transfer and stabilization time; it was the time for the nebulizer to get adapted to the sample viscosity.

6 Wavelength selection and analytical conditions

Table 4: Analytical conditions

Element	Slits (µm)	Analysis mode	Integration time (sec)
Ca	20 x 15	Mean on 3 points	2

7 Discussion

A 4-hour test was undertaken. The results are presented in Table 5 below.

7.1 Stability test with simultaneous internal standard

Table 5 : Stability with simultaneous IS

Ca Sim(Ni)	Conc. (%)	SD	RSD 3 replicates	Time
	45.52	0.0278	0.063	17H57
	45.75	0.0418	0.094	18H11
	45.63	0.062	0.14	18H24
	45.54	0.0393	0.089	18H38
	45.51	0.0663	0.15	18H52
	45.32	0.128	0.29	19H06
	45.29	0.0176	0.04	19H20
	45.37	0.0405	0.092	19H34
	45.22	0.0571	0.13	19H48
	45.40	0.0353	0.08	20H02
	45.20	0.237	0.54	20H16
	45.14	0.032	0.073	20H29
	45.23	0.0922	0.21	20H43
	45.03	0.0267	0.061	20H57
	45.15	0.0482	0.11	21H11
	45.07	0.07	0.16	21H25
	44.87	0.105	0.24	21H39
	45.20	0.0702	0.16	21H53
RSD over 4 hours (%)	0.50			

7.2 Stability test with sequential internal standard

Table 6: Stability test with sequential IS

Ca Seq Ni)	Conc. (%)	SD	RSD 3 replicates	Time
	45.35	0.159	0.35	17H57
	45.37	0.118	0.26	18H11
	45.69	0.142	0.31	18H24
	45.12	0.0906	0.2	18H38
	45.15	0.0635	0.14	18H52
	44.99	0.163	0.36	19H06
	45.60	0.114	0.25	19H20
	44.89	0.171	0.38	19H34
	45.24	0.0908	0.2	19H48
	45.49	0.0822	0.18	20H02
	45.74	0.202	0.44	20H16
	45.41	0.146	0.32	20H29
	45.60	0.105	0.23	20H43
	45.51	0.128	0.28	20H57
	4587	0.0507	0.11	21H11
	45.27	0.0954	0.21	21H25
	45.37	0.164	0.36	21H39
	45.59	0.0824	0.18	21H53
RSD over 4 hours (%)	0.58			

7.3 Analysis the following day

An analysis was undertaken the following day, before and after a recalibration.

Before recalibration:

Ca sim = 44.09 % (RSD = 0.14%)
Ca seq = 45.85 % (RSD = 0.28%)

After recalibration:

Ca sim = 45.56 % (RSD = 0.064%)
Ca seq = 45.39 % (RSD = 0.15%)

7.4 Analysis five days after

Before recalibration:

Ca sim = 46.13 % (RSD = 0.11%)
Ca seq = 45.86 % (RSD = 0.048%)

After recalibration:

Ca sim = 45.37 % (RSD = 0.065%)
Ca seq = 45.45 % (RSD = 0.06%)

8 Conclusion

The use of the internal standard and the operating conditions described in this Application Note enables the user to obtain very good accuracy and precision on a major analyte, even in high salt matrices. The choice of the internal standard is a key point for better precision and accuracy.