Application Note

# Analysis of the Major Elements in Cement by ICP

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## 1 Introduction

Chemical analysis of cement is an interesting application for ICP spectrometry. The cement industry requires analysis of major elements at % levels to very high accuracy and precision, including Si, Ca, Al, Fe and S and also minor elements such as Na, K, Ti, Mg, P, Mn. The trace elements are also very important for environmental pollution control, this includes species like Cr, Pn, Zn, Ni, As, Cd, V and Cu at ppm levels. All these elements are possible by the ICP technique. The use of a combined ICP-AES, such as the ULTIMA 2C, enables fast analysis of all above mentioned elements. For major elements, the repeatability required is in the range 0.2 to 0.5 %, for this reason the simultaneous component is often used for routine analysis, whereas trace elements are better done on the sequential portion for the superior detection limits.

## 2 Principle

### *2.1 Technique used*

The elemental analysis of solutions was undertaken by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). 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 Wavelength choice*

The choice of the wavelength in a given matrix can be made using the "profile" function, or by using Win-IMAGE, which is rapid semi-quantitative analysis mode using multiple wavelengths. The principle is the same in either case: record the scans of analytes at low concentration, and of the matrix. By superimposing the spectra, we see possible interferences.

## 3 Sample Preparation

### *3.1 Classical digestion*

0.1g of sample is fused at 1,000 °C with 1 g of lithium tetraborate for about 30 minutes. The fusion residue is then dissolved with 5 % HCl and made up to a volume of 500 mL.

### *3.2 Microwave digestion*

0.1 g of cement is weighed and 2.5 mL of concentrated $HNO_3$, 2.5 ml $HBF_4$ and 0.5 ml concentrated HCL are added to the sample. The digestion program is 5 minutes at 25 % power and then 5 minutes at 50 % power. The residue is dissolved in 5 % HCl and brought up to a volume of 500 mL.

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## 4.Instrument specification

The work was done on a ULTIMA 2C.The specifications of this instrument are listed below in Tables 1 and 2.

**Table 1: Specification of spectrometer**

| Parameters | Monochromator | Polychromator |
|---|---|---|
| Mounting | Czerny-Turner | Paschen-Runge |
| Focal length | 1 m | 0.5 m |
| Grating number of grooves | 2 400 gr/mm working in 2 orders | 3 600 gr/mm |
| Variable resolution | Yes | No |
| Nitrogen purge | Yes | **Yes** |

**Table 2: Specification of RF Generator**

| Parameters | Specifications |
|---|---|
| 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 | 0.8 L/min |
| Sheath gas flowrate | 0.3 L/min |
| Nebulizer flowrate | 2.51 bars |
| Sample uptake | 0.8 mL/min |
| Type of nebulizer | JY 0.7 |
| Type of spray chamber | Scott |
| Argon humidifier | No |
| Injector tube diameter | 3.0 mm |

## 6 Wavelength selection and analytical conditions

All the lines were measured with the direct peaking mode. The integration time was 2 s for the elements analyzed with the monochromator, and 10 s for the polychromator elements.

**Table 4: Wavelength selection and analytical conditions**

| Element | Wavelength |
|---|---|
| Al | 308.215 |
| As | 189.042 |
| Ca | 317.215 |
| Cd | 228.802 |
| Cr | 267.716 |
| Fe | 259.940 |
| Mg | 279.079 |
| Mn | 257.610 |
| Na | 589.592 |
| Ni | 231.604 |
| Pb | 220.353 |
| S | 180.676 |
| Si | 251.611 |
| Tl | 190.864 |
| Ti | 337.280 |
| V | 292.402 |
| Zn | 213.856 |

## 7 Results

### *7.1 Standard preparation*

The standards were prepared like the samples. For major elements, it is suggested to take at least 4 certified materials. For trace elements, 2 standards are enough. The choice of the standards will depend on the concentration ranges of the samples. For Ca, Si, Fe and Al an internal standard (Li) is required to compensate for the matrix differences.

### *7.2 Analysis of 3 cements on the monochromator*

The cements were measured three times and reported in the table below, with the concentrations expressed in %. The results are presented in Table 5.

### *7.3 Analysis of 3 cements on the polychromator*

The accuracy with the polychromator was as good as for the monochromator, but the precision and repeatability was much better. The results are presented in Table 6.

**Table 5: Analysis of 3 cements on the monochromator**

| Element | 8889 Conc % | 8889 RSD % | Certified % | 9090 Conc % | 9090 RSD % | Certified % | 9191 Conc % | 9191 RSD % | Certified % |
|---|---|---|---|---|---|---|---|---|---|
| $SO_3$ | 2.76 | 1.4 | 2.77 | 1.97 | 0.78 | 2.03 | 3.15 | 1.1 | 3.07 |
| $SiO_2$ | 25.35 | 0.17 | 25.46 | 21.42 | 0.16 | 21.51 | 21.20 | 0.26 | 21.10 |
| $Fe_2O_3$ | 2.82 | 0.33 | 3.02 | 3.79 | 0.19 | 3.95 | 4.05 | 0.48 | 4.19 |
| MgO | 0.705 | 0.23 | 0.73 | 1.02 | 0.13 | 1.04 | 0.694 | 0.32 | 0.71 |
| $Al_2O_3$ | 3.42 | 0.46 | 3.38 | 4.15 | 0.28 | 4.13 | 3.28 | 0.18 | 3.30 |
| CaO | 64.60 | 0.19 | 65.29 | 64.30 | 0.23 | 65.29 | 62.13 | 0.31 | 61.99 |
| Ti | 0.155 | 0.36 | - | 0.195 | 0.51 | - | 0.18 | 0.25 | - |
| $Na_2O$ | 0.088 | 0.51 | 0.09 | 0.17 | 0.42 | 0.13 | 0.134 | 0.70 | 0.12 |
| $K_2O$ | 0.190 | 0.32 | 0.19 | 0.60 | 1.04 | 0.59 | 0.864 | 0.49 | 0.82 |

**Table 6: Analysis of 3 cements on the polychromator**

| Element | 8889 Conc % | 8889 RSD % | Certified % | 9090 Conc % | 9090 RSD % | Certified % | 9191 Conc % | 9191 RSD % | Certified % |
|---|---|---|---|---|---|---|---|---|---|
| $SO_3$ | 2.79 | 0.31 | 2.77 | 2.11 | 0.17 | 2.03 | 3.15 | 0.23 | 3.07 |
| $SiO_2$ | 25.38 | 0.02 | 25.46 | 21.49 | 0.11 | 21.51 | 3.96 | 0.08 | 21.10 |
| $Fe_2O_3$ | 2.78 | 0.09 | 3.02 | 3.86 | 0.04 | 3.95 | 21.27 | 0.07 | 4.19 |
| MgO | 0.69 | 0.17 | 0.73 | 1.02 | 0.07 | 1.04 | 0.702 | 0.24 | 0.71 |
| $Al_2O_3$ | 3.35 | 0.10 | 3.38 | 4.14 | 0.05 | 4.13 | 3.29 | 0.12 | 3.30 |
| CaO | 64.33 | 0.06 | 65.29 | 65.11 | 0.12 | 65.29 | 62.08 | 0.22 | 61.99 |
| Ti | 0.160 | 0.14 | - | 0.202 | 0.07 | - | 0.18 | 0.31 | - |
| $Na_2O$ | 0.092 | 1.1 | 0.09 | 0.16 | 0.36 | 0.13 | 0.131 | 0.61 | 0.12 |
| $K_2O$ | 0.188 | 0.26 | 0.19 | 0.57 | 0.18 | 0.59 | 0.857 | 0.34 | 0.82 |

## 8 Conclusion

It is particularly interesting to point out that HORIBA Scientific ICPs have the ability to analyze any type of sample for example, cements, where there is a high salt content due to alkali fusion. The advantage of the ULTIMA 2C is to simultaneously measure the major and trace elements with very high precision. It also enables you to measure an internal standard at the same time and with the same optics for all major elements, improving the repeatability and accuracy for these elements. The use of the sheath gas device originally patented by JY, enables analysis without clogging of the injector tube and to be able to run samples up to 300 g/L salt content. Given the above criteria, ICP emission spectrometry is suitable for analysis of the major and minor elements in cement.

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