**Challenge**
Analysis of trace elements in complex sample matrix of Portland cement mixture

**Solution**
HR ICP-OES with industry leading high-resolution optical system and superior sensitivity and matrix tolerance to achieve lowest detection limits for trace element analysis in Portland cement

**Intended audience**
Chemical and materials, cement industry, quality control

# Analysis of Trace Elements in Portland Cement Using HR-ICP-OES

## Introduction

Cement is a pivotal material in the construction industry, serving as a binder that unites various components in concrete, mortar, and other mixtures. It is produced from raw materials like calcined lime and clay, which provide the main ingredients calcium oxide, silica, alumina, and iron oxide. Cement manufacturing involves heating these and, with possible additives, transforming them into a fine powder. The composition and properties of cement depend on the type and proportion of these ingredients.[1]
While major ingredients and additives yield the desirable properties of the cement, the presence of trace elements or impurities can lead to undesirable effects, affecting the quality of the final product. For instance, the inclusion of chromium or zinc may alter the color, setting time, and strength of the cement.[2] Beyond compromising the quality of the cement, these trace elements can pose health risks due to their toxic nature.[3] Therefore, monitoring impurities is crucial to ensure the quality and specifications of the cement. The presented method for monitoring involves the detection of trace elements through inductively coupled plasma optical emission spectroscopy (ICP-OES). Achieving high precision and the lowest detection limits is crucial for product control of these elements by ICP-OES. However, the measurements of many trace elements face challenges in detectability due to signal suppression, drifting, and spectral interferences. The latter often necessitate the use of less sensitive alternative lines. The use of High-Resolution Array ICP-OES offers a solution to many of these analytical challenges, providing the means to overcome issues related to signal suppression, drifting, and spectral interferences. The PlasmaQuant 9100 Elite exhibits outstanding analytical potential due to its exceptionally high spectral resolution (2 pm @ 200 nm) and sensitivity. This advanced system enables interference-free analysis of trace elements even in complex matrices such as Portland cement. The robustness of the high-frequency generator and the sample introduction system, featuring the V-Shuttle torch, facilitates the accurate and precise analysis of high-matrix samples. In this study, the PlasmaQuant 9100 Elite was employed to quantify trace elements in reference materials (NIST reference materials SRM 635a Portland cement and SRM 1886b white Portland cement). The analysis also included a QC standard for method validation and long-term stability testing.

# Materials and Methods

## Samples and reagents

- SRM 635a Portland cement (blended with slag)
- SRM 1886b White Portland cement
- Trace metal basis lithium metaborate and lithium tetraborate (Sigma Aldrich)

## Sample preparation

0.15 g of SRM samples were weighed into platinum crucibles. After adding 0.6 g of 1:1 ratio lithium salts, the samples were placed in a muffle furnace set at 1050 °C for 1 hour. Upon completion of the fusion and cooling, the solidified flux was dissolved in diluted nitric acid and filled up to 100 mL volume with deionized water for analysis on the PlasmaQuant 9100 Elite. Matrix matched calibration standards were prepared in diluted nitric acid containing similar concentration of the lithium salts.

## Calibration

Table 1: Concentration of calibration standards

| Parameter | Unit | Cal. 0 | Cal. 1 | Cal. 2 | Cal. 3 | Cal. 4 | Cal. 5 | Cal. 6 |
|---|---|---|---|---|---|---|---|---|
| Ba, Cr, Mn, Sr, Zn | mg/L | 0 | 0.01 | 0.05 | 0.1 | 0.5 | 1 | 2 |

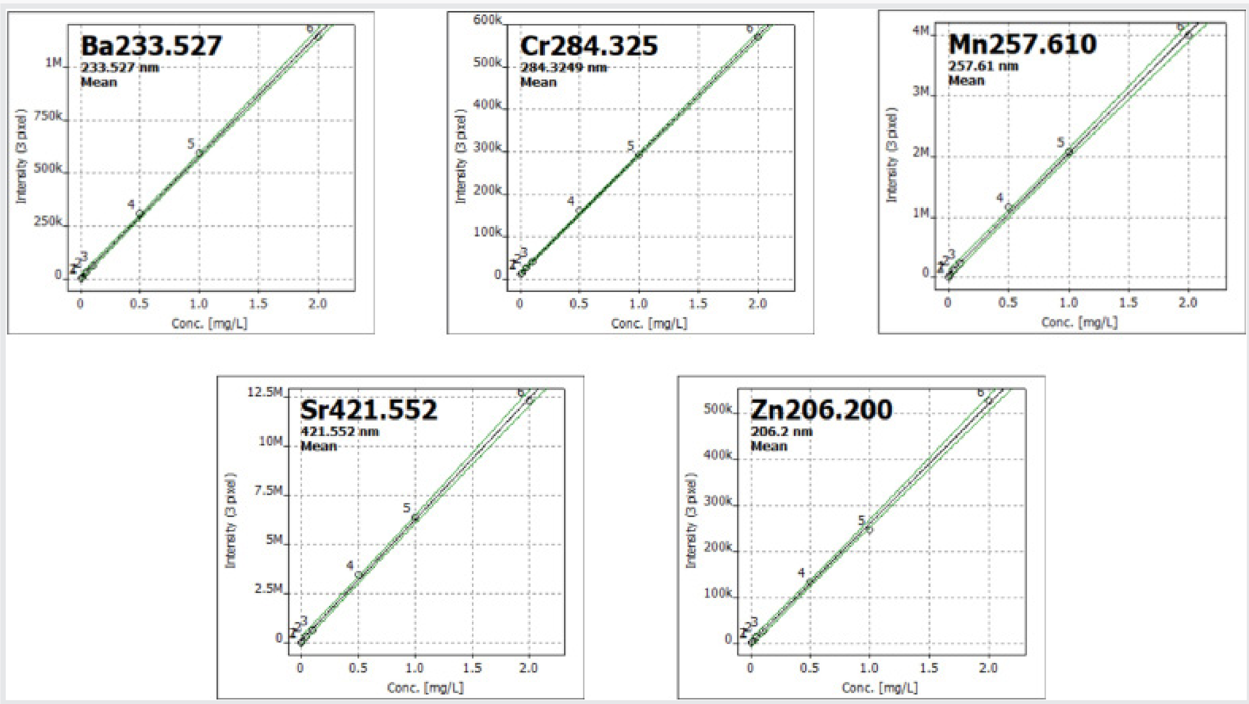


Figure 1: Plots of the matrix matched calibrations

## Instrument Settings

For the analysis, PlasmaQuant 9100 Elite equipped with standard kit and an autosampler was used. The details of the system configuration are given in the Table 2.

Table 2: Plasma and sample introduction system configuration

| Parameter | Specification |
|---|---|
| Power | 1300 W |
| Plasma gas flow | 13 L/min |
| Auxiliary gas flow | 0.65 L/min |
| Nebulizer gas flow | 0.55 L/min |
| Nebulizer | concentric nebulizer for high salt content, 1 mL/min |
| Spray Chamber | cyclonic (50mL) |
| Outer/inner tube | quartz/quartz |
| Injector | quartz, 2 mm |
| Pump tubing | PVC |
| Sample pump rate | 1.0 mL/min |
| Delay time | 45 sec |

## Method Parameters

Table 3: Method parameters

| Element | Line | Plasma view | Integration | Read time [s] | Evaluation | | |
|---|---|---|---|---|---|---|---|
| | | | | | Pixel | Baseline fit | Poly. deg. |
| Ba | 233.527 | Atten. axial[+] | Peak | 3 | 3 | ABC[1] | auto |
| Cr | 284.325 | Atten. axial | Peak | 3 | 3 | ABC | auto |
| Mn | 257.610 | Atten. axial | Peak | 3 | 3 | ABC | auto |
| Sr | 421.552 | Atten. axial | Peak | 3 | 3 | ABC | auto |
| Zn | 206.200 | Atten. axial | Peak | 3 | 3 | ABC | auto |

[+] attenuated axial view
[1] automatic baseline correction

## Results and Discussion

The following Table 4 shows the concentrations obtained for the trace elements against the certified values of the SRMs. The recoveries range between 92 and 107 %. To check the long-term stability of the instrument, the calibration standard 4 (0.5 mg/L) was used as quality control (QC) and measured after 1 hour of analysis time. The results are shown in Table 5.

Table 4: SRM measurements and recoveries

| Element | SRM 635a | | Integration | SRM 1886b | | Recovery [%] |
|---|---|---|---|---|---|---|
| | Certified Value [m-%] | Measured Value [m-%] | | Certified Value [m-%] | Measured Value [m-%] | |
| Ba as (BaO) | 0.0315 | 0.0289 | 92 | 0.009 | 0.0096 | 107 |
| Cr as ($Cr_2O_3$) | 0.0101 | 0.0102 | 101 | 0.0040 | 0.0040 | 100 |
| Mn as ($Mn_2O_3$) | 0.1279 | 0.1284 | 100 | 0.0264 | 0.0265 | 100 |
| Sr as (SrO) | 0.1754 | 0.1830 | 104 | 0.0886 | 0.0952 | 107 |
| Zn as (ZnO) | 0.0262 | 0.0250 | 95 | | | |

Table 5: QC recovery values after 1 hour

| Element | Measured conc. QC [mg/L] | Recovery [%] |
|---|---|---|
| Ba | 0.55 | 110 |
| Cr | 0.54 | 108 |
| Mn | 0.53 | 106 |
| Sr | 0.52 | 104 |
| Zn | 0.54 | 108 |

## Summary

Maintaining optimal cement specifications is vital not only for compliance with intended applications but also for preventing the release of harmful heavy metals into the air. Consequently, the monitoring of these toxic elements poses a challenging application in cement quality control.
While conventional ICP-OES systems grapple with analytical challenges, including sensitivity requirements, matrix-based spectral interferences, and plasma robustness for matrix-rich samples, the PlasmaQuant 9100 Elite effortlessly masters this demanding application. Features like the high-frequency generator and the V-Shuttle torch design contribute to outstanding plasma robustness in both short- and long-term stability. Achieving QC recovery values of 100% ± 10% after one hour of continuous analysis on cement samples underscores the system's reliability. Leveraging the Dual View Plus plasma viewing feature of PlasmaQuant 9100 enables the combination of highly sensitive analysis for trace elements with high-concentration main component measurements in a single method. The PlasmaQuant 9100 Elite is an ideal instrument for control laboratories in the cement industry and offers a combination of high analytical performance, user-friendly operation and efficient data processing,including automated background correction.

Figure 2: PlasmaQuant 9100 Elite

### Recommended device configuration

Table 6: Overview of devices and consumables

| Article | Article number | Description |
|---|---|---|
| PlasmaQuant 9100 Elite | 818-09101-2 | High resolution ICP-OES |
| Standard Kit for PlasmaQuant 9100 Series | 810-88006-0 | Standard Kit |
| Concentric nebulizer for high salt content 1mL/min Borosilicate glass | 418-13-410-484 | Nebulizer for samples with high salt content |
| Autosampler ASPQ 3300 for ICP-OES or similar | 810-88002-0 | Autosampler |

#### References

[1] Dunuweera S.P and Rajapakse R.M.G.; Cement Types, Composition, Uses and Advantages of Nanocement, Environmental Impact on Cement Production, and Possible Solutions. Advances in Materials Science and Engineering Volume 2018, Article ID 4158682, pages 1-11

[2] I Fernández Olmo, E Chacon, A Irabien; Influence of lead, zinc, iron (III) and chromium (III) oxides on the setting time and strength development of Portland cement. Cement and Concrete Research Volume 31. Issue 8; 2001, pages 1213-1219

[3] SCIENTIFIC COMMITTEE ON TOXICITY, ECOTOXICITY AND THE ENVIRONMENT (CSTEE); Opinion on Risks to Health from Chromium VI in Cement. 32th CSTEE plenary meeting, 27 June 2002



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Version 1.0 · Author: SuRe, KiSc
en · 02/2024