

Ore Grading with LA-ICPMS

Dig Deeper

Current Situation

Presently, divergent methods are set in place to analyze your dirt. One sample is sent to the lab located at the mine. Samples are analyzed and time to result is greatly limited due to the extensive sample preparation required. Digesting samples in acid can take up to 12 hours per sample.

After the XRS process, samples are dissolved in harmful and expensive acids in order to provide the trace element composition. Dissolving samples is a time-consuming procedure and it might take multiple types of acid to determine elemental composition. While examining platinum group elements, customers use the hazardous process of fire assay by extracting the PGE's into a button of lead.

Solution

Laser ablation has a place in commercial, industrial, high throughput laboratories. The technique and equipment has evolved since inception to allow accurate and consistent results. Time to result is crucial during this step of analysis because the digging process is on hold until lab results are clear. Macro laser ablation allows for bulk analysis. Macro produces precise answers that are representative of the distribution of each sample. Laser ablation can replace current methods with one consistent process. Once an infrastructure is in place, continuous analysis is key to ensure profitability.

Unlike current methods, laser ablation makes sequential analysis possible. Each sample is analyzed individually making time to result goals consistent and short. After samples are sent to the lab, XRF and laser ablation can be used as complimentary techniques simultaneously determining major and trace element concentration.



Introduction

Despite the fact that the availability of good quality, solid certified reference materials has increased dramatically in recent years, one major limitation of quantitative analysis by LA-ICPMS is the lack of CRMs for some sample types. 'In house' solid synthetic standards are often prepared to allow external calibration; however, with such external standards it is especially important that the standard matches the sample in terms of matrix composition, since even a small difference in composition can lead to vastly different rates of ablation. This is especially important as no internal standard element is present in both the sample and standard to correct for these different ablation yields.

This work describes the utilization of an actively absorbing binder, vanillic acid, that when mixed with the sample (60% Sample: 40% Binder) significantly improves the ablation efficiency and reduces the matrix dependency of the process, thus improving the accuracy of calibration using non-matrix matched external calibration.

The calibration strategy defined in this application note particularly lends itself to bulk analysis of trace elements within powdered samples such as soils, sediments, foodstuffs and cosmetics

Methods

- 1a. Weigh out 0.24g of sample and 0.16g of vanillic acid into a 25ml polystyrene sample vial.
- 1b. At this point it is also possible to spike the mixture with a small volume (50 μ L) of an aqueous spike for internal standard addition or isotope dilution. The mixture should be dried for 1 hour at 60°C. This step is optional.
2. Add two 9mm OD polyamide beads.
3. Homogenize for 15 min at 30 Hz in a Retsch MM200 mixer mill.
nb. A pestle and mortar can be utilized, but homogeneity will be compromised.
4. Transfer 0.25g of the resulting mixture to a standard IR press equipped with 13mm dyes.
5. Press for 5 min under 10 tons of pressure to yield discs of 13mm OD and 1.2mm thickness.
6. Analyze discs by LA-ICPMS using the parameters described in Table 1.

Table 1. Instrumental parameters

| LA System | NWR213* |
|------------------|---------------------|
| Fluence | 2 J/cm ² |
| Spot size | 110 μ m |
| Scan speed | 10 μ m/s |
| Frequency | 20 Hz |
| He flow rate | 0.9 L/min |
| Air flow rate | 0.8 L/min |
| ICPMS | Quadrupole ICPMS |
| Forward Power | 1400 W |
| Ar gas flow rate | 0.95 L/min |
| Dwell time/m/z | 0.01-0.1 s |

*Now ESL213

The discs were analysed by LA-ICPMS using a rastering sampling strategy. The recovery (or % accuracy) and precision (%RSD) were determined by performing multiple single point calibrations. In order to determine the relationship between data quality and the degree of matrix matching, calibration was performed using different combinations of discs as sample and calibration standard. The results are demonstrated in Table 2.

Table 2. Results demonstrating accuracy and precision with varying disc composition.

| Sample | Standard | Recovery (100% CRM)% | | Recovery (40% PVA)% | | Recovery (40% Vanillic)% | |
|----------|----------|----------------------|-----|---------------------|-----|--------------------------|-----|
| | | Mean | RSD | Mean | RSD | Mean | RSD |
| IMEP14 | GBW07311 | 177 | 17 | 183 | 19 | 93 | 10 |
| GBW07401 | GBW07311 | 115 | 23 | 125 | 55 | 110 | 12 |
| GBW07311 | IMEP14 | 69 | 15 | 49 | 20 | 104 | 24 |
| GBW07401 | IMEP14 | 59 | 18 | 75 | 55 | 111 | 15 |
| GBW07311 | GBW07401 | 92 | 24 | 130 | 71 | 98 | 7 |
| IMEP14 | GBW07401 | 174 | 37 | 149 | 41 | 94 | 11 |
| Mean | Mean | 114 | 22 | 119 | 44 | 102 | 13 |
| SD | SD | 51 | | 49 | | 8 | |
| %RSD | %RSD | 45 | | 41 | | 8 | |

Conclusions

Employing vanillic acid as a binder introduces a degree of matrix matching between sample and standard, but more importantly, standardizes the absorptivity of the matrix. This in turn leads to a standardization of ablation conditions and mass flux to the plasma which are prerequisites for robust calibration.

Unlike the use of a traditional, nonabsorbing binder, which simply dilutes the sample, this matrix matching is accompanied by an increase in sensitivity. The result is a substantial improvement in the quality of data obtained when using external calibration for LA-ICPMS.

The use of the pressed powders standard preparation method has been shown to offer a robust calibration method for the quantitative analysis of powdered samples using simple external calibration. The data produced would be fit-for-purpose in many practical analytical applications. The technique is simple and employs commonly available laboratory reagents and equipment.

Reference

Ciaran O' Connor, Mark R. Landon and Barry L. Sharp, Absorption Coefficient Modified Pressed Discs for Calibration of Laser Ablation Inductively Coupled Plasma Mass Spectrometry, Journal of Analytical Atomic Spectrometry, 2007, 22, 273-282



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