Introduction

The analysis of geological materials by ICP-MS presents several challenges: low analyte levels, unusual interferences and high total dissolved solids (TDS). Each of these characteristics can potentially cause a problem for ICP-MS analysis.

Low analytical levels require high sensitivity and a low background equivalent concentration (BEC) at the analytical mass of interest. The presence of unusual interferences can cause elevated BECs, making low-level determinations impossible. The interfering species arise from unique matrix components and are unusual in that they are not commonly encountered in ICP-MS analyses outside geological samples. The presence of high TDS can cause instrumental drift as well as high BECs, if deposited materials re-ionize.

However, the ELAN® DRC II can address all of these limitations. Design characteristics of the ELAN DRC II limit solids deposition, instrument drift and re-ionization of deposited materials. By incorporating a Dynamic Reaction Cell™ (DRC™), the effects of unusual interferences can be removed through the selection of the most effective reaction gas for interference removal, used in combination with dynamic band-pass tuning (DBT). As a result, the effects of interferences are eliminated without sacrificing analyte sensitivity, allowing low-level analyte determination.

Geological Analyses with the ELAN DRC II

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**Experimental**

**Instrumental conditions**

All analyses were performed on an ELAN DRC II (PerkinElmer SCIEX™, Concord, Ontario, Canada). General operating conditions for each analysis are given in Table 1, and specific conditions are discussed later.

**Sample preparation**

Simulated matrices were made from 1,000 or 10,000 mg/L single-element standards (PE Pure, PerkinElmer Life and Analytical Sciences, Shelton, CT USA; Spex, Metuchen, NJ USA) diluted in 18 MΩ water and high-purity nitric and/or hydrochloric acids (GFS Chemicals, Columbus, OH USA; Optima Grade, Fisher Scientific, Pittsburgh, PA USA).

For lithium metaborate fusion tests, a certified reference material (BEN, basalt rock) was used. This sample was received already digested (from a third party) and was simply diluted prior to analysis. Other geological materials analyzed were received in solution and diluted prior to analysis. All dilutions were made with 1% nitric acid.

**Results and discussion**

**Lithium metaborate fusion**

The analysis of lithium metaborate fusion samples by ICP-MS is challenging because of the high lithium content of the samples – about 200 mg/L entering the instrument. Although this concentration is not excessively high for ICP-MS, lithium (Li) is a notoriously “sticky” element in that it may deposit on interface components, which can lead to signal drift.

Prior to analysis, the ELAN DRC II was conditioned by continuous aspiration of a simulated lithium metaborate fusion matrix with TDS concentration of 200 mg/L. This step established a uniform matrix coating on the lens and cones. The lens voltages were then calibrated in this matrix.

A fused geological standard reference material was diluted to give a final TDS concentration of 200 mg/L (0.02% TDS). This sample was analyzed in standard mode (i.e., no reaction gas used) over 8 hours, with measurements made every 8 minutes. Figures 1-4 show the measured concentrations of elements present at < 1 µg/L, 1-10 µg/L, 10-100 µg/L and 100-400 µg/L, respectively. The data in these figures demonstrate that even though a wide concentration range was measured, the results were stable over 8 hours. Further evidence of the stability is presented in Figure 5, where the normalized rhodium signal (internal standard at 20 µg/L) is plotted over the same 8-hour analysis time. Even in such a difficult matrix, the rhodium intensity decreases by only 25%, further demonstrating minimal deposition within the instrument.

**Lithium deposition and re-ionization**

Because lithium is a sticky element and deposits readily on instrument components, a test was performed to determine if Li deposition leads to higher Li background signals in subsequent analyses. This could be a significant problem because Li has a low first-ionization potential (5.4 eV) which facilitates re-ionization of deposited Li, leading to higher BECs. These characteristics are important if an instrument which runs lithium metaborate fusion analyses will also be used for trace Li measurements in other samples.

To test the effect of Li deposition and re-ionization, a 100-mg/L Li solution spiked with 10 µg/L of indium (In), barium (Ba), lead (Pb) and uranium (U) was aspirated continuously for four hours. During this time, the intensities of the spiked elements were measured every 5.5 minutes in standard mode. Figure 6 shows a stability plot of these elements (intensities normalized to the first reading at the beginning of the analysis), as well as the relative standard deviations over the four hours.
Figure 1. Eight-hour stability of elements present at < 1 µg/L in a lithium metaborate fusion sample (BEN basalt rock).

Figure 2. Eight-hour stability of elements present between 1-10 µg/L in a lithium metaborate fusion sample (BEN basalt rock).

Figure 3. Eight-hour stability of elements present between 10-80 µg/L in a lithium metaborate fusion sample (BEN basalt rock).

Figure 4. Eight-hour stability of elements present between 100-400 µg/L in a lithium metaborate fusion sample (BEN basalt rock).

Figure 5. Eight-hour stability of a 20 µg/L Rh spike in a lithium metaborate fusion sample (BEN basalt rock).

Figure 6. Four-hour stability of 10 µg/L spike in a 100 mg/L lithium solution (continuous aspiration) and %RSD.
hours. Excellent stability is demonstrated by the low RSDs over four hours (≤ 3.25%) and the small signal drift (±10%).

To check for Li deposition within the instrument, the Li BEC was measured in 1% HNO₃ prior to aspiration of the Li matrix and was found to be 2.5 ng/L. After Li aspiration, the following sample-introduction components were replaced by new, identical components: sample-uptake tubing, nebulizer, spray chamber, injector, torch, sampler cone and skimmer cone. This replacement was done to eliminate memory effects of the sample introduction system and check for memory effects only from deposition within the instrument.

With the new sample-introduction components, the instrument was allowed to warm up for ten minutes and the Li BEC measured again. This BEC was found to be 2.7 ng/L – virtually identical to that determined before lithium matrix aspiration. This result indicates that Li does not re-ionize significantly within the ELAN, meaning that by only cleaning or changing sample-introduction components, trace Li analyses can be performed after lithium metaborate fusion analyses.

Instrumental design considerations

The stability and lack of deposition within the ELAN directly result from design characteristics of the instrument. The primary reason is the lens system used in the ELAN: a single scanning lens with a grounded shadow stop, as shown in Figure 7. The single lens is simple to maintain and clean. Additionally, the optimum lens voltage for maximum transmission differs with m/z, as shown in Figure 8. The advantage of this scheme is that transmission of matrix species through the lens is minimized when measuring an analyte at a significantly different m/z. This unique characteristic limits the amount of Li passing through the lens when other elements are being measured. Therefore, it is a significant factor in preventing deposition within the system.

The implementation of a grounded shadow stop also inhibits re-ionization and drift: the matrix hits the shadow stop and sticks so that no re-ionization occurs. If a voltage were applied to the shadow stop, re-ionization would be encouraged, similar to the effect seen with extraction lenses. Another benefit of the shadow stop is that it keeps the matrix from entering the ELAN. This results in greater stability in high-matrix samples.
reaction cell clean by blocking matrix species and preventing them from entering the cell.

Eliminating interferences in a nickel-copper-chloride (Ni-Cu-Cl) matrix

A common matrix encountered in the copper mining and processing industries contains high levels of nickel, copper and chloride, which result from digestion of copper ores in hydrochloric acid. To determine the purity of a product, low levels of many elements must be determined in this matrix. Particularly problematic are rhodium (Rh), ruthenium (Ru) and palladium (Pd), which suffer from Ni-Cu-Cl interferences on all the major isotopes, as shown in Table 2. After sample preparation and dilution, the following matrix is introduced to the ELAN: 80 mg/L Ni + 40 mg/L Cu + 1% HCl. Desired analyte levels are < 0.5 µg/L.

The ELAN DRC II can perform this analysis using ammonia as a reaction gas to eliminate the interferences on Ru, Rh and Pd. Figures 9-11 show ammonia reaction profiles acquired with the appropriate DBT settings. In these figures, the green line is the signal from the matrix (described above) and the blue line is the signal from the matrix spiked with 0.5 µg/L of analyte. The red line in each plot shows the BEC. In all cases, the matrix signal is eliminated or reduced significantly, while the signal from the analytes remains strong. As a result, BECs are ≤ 10 ng/L, allowing low levels of Ru, Rh and Pd to be measured in the Ni-Cu-Cl matrix.

Figure 9. Ammonia optimization for ^{101}Ru (0.5 µg/L) in a matrix composed of 80 mg/L Ni + 40 mg/L Cu + 1% HCl. The green line is the signal from the matrix; the blue line is the signal from the matrix + 0.5 µg/L Ru spike; the red line represents the background equivalent concentration. RPq = 0.75

Figure 10. Ammonia optimization for ^{103}Rh (0.5 µg/L) in a matrix composed of 80 mg/L Ni + 40 mg/L Cu + 1% HCl. The green line is the signal from the matrix; the blue line is the signal from the matrix + 0.5 µg/L Rh spike; the red line represents the background equivalent concentration. RPq = 0.75

Figure 11. Ammonia optimization for ^{105}Pd (0.5 µg/L) in a matrix composed of 80 mg/L Ni + 40 mg/L Cu + 1% HCl. The green line is the signal from the matrix; the blue line is the signal from the matrix + 0.5 µg/L Pd spike; the red line represents the background equivalent concentration. RPq = 0.75
Determination of gold, platinum and palladium in digested rock

In the mining industry, it is important to measure low levels of precious metals. Palladium (Pd), gold (Au) and platinum (Pt) are metals of interest, but they suffer from zirconium (Zr), tantalum (Ta) and hafnium (Hf) oxide interferences, which originate from matrix species. Even though the interfering elements may be present at low levels, they readily form oxides which cause significant interferences on Pd, Au and Pt.

To overcome the interference problem, methylfluoride (CH₃F) is used as a reaction gas in two ways: first, to eliminate the interfering species and second, to react with the analyte to form a new analytical species at a higher mass, away from the interferences. It was found that Au and Pt both react readily to form new species (AuCH₃F⁺ at m/z 231 and PtCHF⁺ at m/z 226), while ZrO⁺ reacts with CH₃F and is eliminated. Evidence of these reactions appears in Figures 12-14. In these figures, a synthetic matrix was made to mimic what might be found in a digested rock, after dilution: 2 µg/L of Ta and Hf + 200 µg/L Zr + 0.5% HCl + 0.33% HNO₃. Palladium, gold and platinum were then spiked at 0.5 µg/L. In each case, the signal from the matrix is greatly reduced, while that from the 0.5-µg/L spike remains high, leading to BECs of less than 10 ng/L.

The conditions established were then applied to the analysis of a digested rock sample (prepared by a third party). Table 3 lists the instrumental and reaction-cell conditions used for the analysis, and Table 4 displays the results. The first row of Table 4 shows the supplied results, which were obtained by conventional ICP-MS. The second row displays the

Figure 12. Methylfluoride optimization for ¹⁰⁵Pd (0.5 µg/L) in a matrix composed of 2 µg/L Ta + 2 µg/L Hf + 200 µg/L Zr + 0.5% HCl + 0.33% HNO₃. The green line is the signal from the matrix; the blue line is the signal from the matrix + 0.5 µg/L Pd spike; the red line represents the background equivalent concentration. RPq = 0.65

Figure 13. Methylfluoride optimization for AuCH₃F (m/z 231; 0.5 µg/L) in a matrix composed of 2 µg/L Ta + 2 µg/L Hf + 200 µg/L Zr + 0.5% HCl + 0.33% HNO₃. The green line is the signal from the matrix; the blue line is the signal from the matrix + 0.5 µg/L Au spike; the red line represents the background equivalent concentration. RPq = 0.70

Figure 14. Methylfluoride optimization for PtCHF (m/z 226; 0.5 µg/L) in a matrix composed of 2 µg/L Ta + 2 µg/L Hf + 200 µg/L Zr + 0.5% HCl + 0.33% HNO₃. The green line is the signal from the matrix; the blue line is the signal from the matrix + 0.5 µg/L Pt spike; the red line represents the background equivalent concentration. RPq = 0.75
results obtained with the ELAN DRC II. Comparing these two rows shows that the DRC results are much lower than those obtained by conventional ICP-MS, demonstrating that the interferences are reduced or eliminated. The sample was then spiked with 0.2 µg/L of analytes and analyzed again. The results appear in row three of Table 4 and demonstrate good recovery.

To further test the extent of interference removal with the DRC, the spiked sample was spiked again with 100 µg/L of Zr, Ta, and Hf. This level is 50 times higher than expected for Ta and Hf and increases the Zr concentration by 50%. The sample was then analyzed, and the results appear in the last row of Table 4. Even though the interference levels are much higher than in the original sample, the measured concentrations of Pd, Au, and Pt are virtually identical to those measured without the interference spike. These results demonstrate that the interference effects are eliminated.

**Conclusions**

This work has shown that the ELAN DRC II can be used to successfully analyze geological samples by overcoming many of the difficulties presented by this type of matrix. Instrument design characteristics make the ELAN DRC II unique with the capability of handling high dissolved solids with minimal drift or sample deposition. The incorporation of Dynamic Bandpass Tuning allows a wide variety of reaction gases to be selected, so that the best gas for a particular application can be used. This fact is important since geological samples produce many interferences not normally encountered in typical ICP-MS applications. The flexibility to use the most appropriate reaction gas means that the effects of interferences can be greatly reduced or completely eliminated. As a result of these characteristics, the ELAN DRC II is an ideal tool for trace metal determinations in geological matrices.

<table>
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<tr>
<th>Analyte</th>
<th>Interference</th>
<th>Analytical Species</th>
<th>m/z</th>
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* Customer supplied values determined by conventional ICP-MS
* Interference Spike = 100 µg/L Zr, Hf, Ta