Analytical evaluation and analysis of geological samples and possible method validation

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Abstract

Among the goals of analytical chemistry is improving established analytical methods, extending existing methods of analyses to new types of samples, and developing new methods to analyse new types of samples with complex matrices. Geological samples often include a wide range of matrices and elements at differing concentrations, from trace elements to major components. Besides this, various inter-element interferences can occur and must be taken into consideration when analysing such samples. This makes analyses of this type of samples an uneasy one, requiring different preparation and analytical methods. The best possible applicable methods and procedures for sample preparation and the instrumental techniques required for the analysis of these type of samples were under exhaustive evaluation. After exploring suitable digestion methods, various analytical techniques i.e. ICP-MS, ICP-OES, XRF and combustion were used for the analyses of possible 51 elements on the samples. Soil international certified reference materials (CRMs) were used for method development and for quality assurance before analysing real geological (soil) samples. Good recoveries were obtained for all of 51 elements (major and trace) present in the soil CRMs, data obtained also shown good repeatability (RSD < 10). Results on real samples analysed showed a good correlation with data from an external laboratory. Therefore, this paper details how analyses were conducted, optimization of methods to suits types or matrices of the samples up to method validation step.

1. Introduction

Geological materials including rocks and minerals present a puzzle pieces that contain important information about particular geological environments, and this information can be extremely useful for studies such as determining mineral provenance, reservoir description, prospecting, and geochemical mapping [1]. Geological samples are generally composed of a wide range of elements the analysis method for such unknown samples requires flexibility in their analysis and in addition to speed for the result. Comprehensive investigations of geological samples can be challenging due to variations in sample size, shape, structure and composition. Therefore, it is difficult to use a single analytical technique to obtain an ideal result, because the multielements have a large range of concentration variations. As a result, a combined detection with different analytical methods is a better way for simultaneously analyzing these multi-elements [2, 3]. The need for quick determination of multi-elements
present in geological samples has been increasing for mining and mineral industries, since this gives valuable information of the mineral.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) and ICP-mass spectrometry (ICP-MS) are being used increasingly for the analysis of a wide range of geological materials [4]. The rapidity of these multi-element analytical techniques results are depended on the complete sample dissolution being the determining step in sample throughput. Various method to dissolve the geological sample are well known and frequently used such as acid digestion and fusion methods. X-ray fluorescence (XRF) analysis, which is widespread in metallurgical and processing industries and is used to identify and measure the concentration of the elements in ores and minerals [5]. Sample preparation in XRF technique is not as complex as in ICP analysis for the geological samples.

In this study, acid digestion methods using aqua regia and four acids methods were used to digest the geological samples for both ICP-OES and ICP-MS analysis, and the concentrations of 9 elements were determined by the ICP-OES, 41 elements by the ICP-MS. Pellets were also prepared for XRF analysis. Two soil certified reference materials, OREAS 45e and OREAS 45f were used to develop and optimize a method for geological samples. Good recoveries were obtained for all of 51 elements (major and trace), data obtained had shown good repeatability. Real geological samples were also analysed in the same manner as certified reference materials and the data was compared with external laboratory data.

This paper will only focus on the ICP-MS technique and report on the analysis of 35 out of 41 elements demonstrating the ability of the technique in analyzing the geological samples. The other 6 elements did not have certified values reported on the certificates.

2. Experimental procedures

2.1 Sample preparation methods

A certain amount of crushing and grinding is usually required to decrease the particle size of solid samples. Because these operations tend to alter the composition of the sample, the particle size should be reduced no more than is required for homogeneity and ready attack by reagents. In this exercise, certified reference materials (90% passing 75 μm) and real samples were analyzed as received with no further milling or pulverizing.

2.1.1 4-acid digestion for ICP-MS analysis

For the digestion of samples, analytical grade hydrochloric (HCl), nitric (HNO₃), perchloric (HClO₄) and hydrofluoric (HF) acids were used. Ultra-pure water (18.2 MΩ cm), prepared with a Microsep direct-pure water purifier, was used in the preparation of standard solutions and the final dilution of digested samples.

The sample preparation method was adapted from a multi-acid digestion technique used by the United States Geological Survey [6] and the old Mintek 4-acid digestion method in practice. Test portions of 0.20 g of the sample material were mixed sequentially with 3 ml conc. HCl, 2 ml conc. HNO₃, 1 ml conc. HClO₄ and 2 ml conc. HF in Teflon beakers, and allowed any reaction to subside. After refluxing the mixture for 1.5 h, it was evaporated to incipient dryness. Then 1 mL conc. HClO₄ was added and the sample was evaporated to complete dryness. After cooling 1 ml conc. HNO₃ and two drops of H₂O₂ were added, then 19 ml of 1% HNO₃ was
added and the sample was heated to dissolve the residue. After cooling, the sample was transferred into a 200 ml volumetric flask and diluted to volume with 1% HNO₃. A sample reagent blank was prepared in the same way as the samples.

For ICP-MS analyses, sample dilution was carried out directly into 10 ml vials by pipetting a 2 ml aliquot of the prepared sample and adding 100 μl of a prepared internal standard solution (1 mg/l Iridium in 2% v/v HNO₃). The final volume was made up to 10 ml by ultra-pure water.

### 2.1.2 Aqua regia digestion for ICP-MS for Au, PGMs and Ag analysis

For Au, Ag, Pd and Pt analysis samples were digested in aqua regia as follow: 10 g of sample was mixed with 75 ml of conc. HCl and 25 ml of conc. HNO₃. The mix was allowed to reflux on a hot plate for *ca.* 40-50 min., with frequent gentle swirling to prevent formation of crust at the bottom of the beaker. After cooling, the samples were directly filtered into 200 ml volumetric flasks and filled up to mark with ultra-pure water. A sample reagent blank was prepared in the same way as the samples.

Sample dilution was carried out directly into 10 ml vials by pipetting a 2 ml aliquot of the prepared sample and adding 100 μl of an internal standard solution (1 mg/l Iridium in 2% v/v HCl). The final volume was made up to 10 ml by ultra-pure water.

### 2.2 Standard preparation method

The calibration solutions for quantitative analysis were prepared from several single element standard solutions. The calibration was performed using nine standard solutions as well as a calibration blank and quality control (QC) solutions. The standard solutions were prepared in 2% v/v HNO₃ to match the final sample acid matrix, with 10 ng/ml Ir added as an internal standard. Standard solutions 1, 2 and 3 contained 2, 20 and 80 ng/ml of the following elements: As, Ba, Cd, Co, Cu, Li, Mo, Ni, Pb, Rb, Sr, Te, Tl, U, V and Zn. Standard solutions 4, 5 and 6 contained 2, 10 and 80 ng/ml of Bi, Ce, Cs, Ga, Ge, Hf, In, La, Nb, Re, Sb, Sc, Se, Ta, Th, Y and Zr. Standard solutions 7, 8 and 9 contained 2, 10 and 80 ng/ml of Sn and W.

The calibration for Au, Pd, Pt and Ag was performed using five standard solutions as well as a calibration blank and quality control (QC) solutions. The standard solutions were prepared in 2% v/v HNO₃ to match the final sample acid matrix, with 10 ng/ml Ir added as an internal standard. Standard solutions 1, 2, 3, 4 and 5 contained 1, 5, 10, 40 and 50 ng/ml.

### 2.3 ICP-MS Technique

A Thermo Icap Q ICP-MS equipped with a Perfluoroalkoxy (PFA) nebulizer, a quartz spray chamber and 2.5 mm internal diameter quartz injector, was used for this work. The spray chamber filters out larger aerosol droplets for improved signal stability and low oxide rates. The spray chamber is also cooled using a Peltier cooled chiller to improve instrument performance. The torch consists of two concentric quartz tubes, each with variable flow rates. The gas stream through the outer tube of the torch shapes the plasma and shields the torch body against high temperatures of the plasma. The auxiliary gas flows through the inner tube. The ICP-MS performance was checked regularly and optimised according to the manufacturer’s recommendations (i.e. optimization of nebuliser gas flow and mass calibration). The instrument operating conditions are shown in Table 1 below.
Table 1: Thermo Icap Q ICP-MS operating conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample uptake Rate</td>
<td>1 mL/min</td>
</tr>
<tr>
<td>RF Power</td>
<td>1450 watts</td>
</tr>
<tr>
<td>Nebulizer gas flow</td>
<td>0.98 mL/min</td>
</tr>
<tr>
<td>RPq</td>
<td>0.45 (all isotopes)</td>
</tr>
<tr>
<td>Operating mode</td>
<td>No gas / STD mode and He gas / KED mode</td>
</tr>
</tbody>
</table>

3 Results and discussions

3.1 ICP-MS results

Table 2 and 3 summarizes results for replicate analyses of OREAS 45e and OREAS 45f soil CRMs respectively using different techniques for different elements. Multi-acid digested and aqua regia digested samples analysed by ICP-MS.

Table 2: Statistical evaluation of results obtained using various preparation procedures and various techniques for OREAS 45e soil CRM

<table>
<thead>
<tr>
<th>Element (Isotope)</th>
<th>Certified value, mg/kg</th>
<th>Measured average (n = 20), mg/kg</th>
<th>Recovery, %</th>
<th>RSD, %</th>
<th>LOD, ng/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (107)</td>
<td>0.311</td>
<td>0.35</td>
<td>113</td>
<td>9</td>
<td>0.01</td>
</tr>
<tr>
<td>Au (197)</td>
<td>0.050</td>
<td>0.048</td>
<td>91</td>
<td>15</td>
<td>0.002</td>
</tr>
<tr>
<td>As (75)</td>
<td>16.3</td>
<td>14.46</td>
<td>89</td>
<td>9</td>
<td>0.069</td>
</tr>
<tr>
<td>Ba (136)</td>
<td>252</td>
<td>258</td>
<td>102</td>
<td>7</td>
<td>0.043</td>
</tr>
<tr>
<td>Be (9)</td>
<td>0.62</td>
<td>0.52</td>
<td>84</td>
<td>8</td>
<td>0.01</td>
</tr>
<tr>
<td>Bi (209)</td>
<td>0.28</td>
<td>0.23</td>
<td>82</td>
<td>7</td>
<td>0.005</td>
</tr>
<tr>
<td>Ce (140)</td>
<td>23.5</td>
<td>21.3</td>
<td>91</td>
<td>8</td>
<td>0.04</td>
</tr>
<tr>
<td>Co (59)</td>
<td>57</td>
<td>60.2</td>
<td>106</td>
<td>7</td>
<td>0.085</td>
</tr>
<tr>
<td>Cs (133)</td>
<td>1.26</td>
<td>1.11</td>
<td>88</td>
<td>7</td>
<td>0.123</td>
</tr>
<tr>
<td>Cu (63)</td>
<td>780</td>
<td>707</td>
<td>91</td>
<td>9</td>
<td>0.005</td>
</tr>
<tr>
<td>Ga (69)</td>
<td>16.5</td>
<td>18.5</td>
<td>112</td>
<td>16</td>
<td>0.002</td>
</tr>
<tr>
<td>Hf (178)</td>
<td>3.11</td>
<td>3.15</td>
<td>101</td>
<td>5</td>
<td>0.001</td>
</tr>
<tr>
<td>In (115)</td>
<td>0.099</td>
<td>0.10</td>
<td>100</td>
<td>7</td>
<td>0.005</td>
</tr>
<tr>
<td>La (139)</td>
<td>11</td>
<td>9.03</td>
<td>82</td>
<td>12</td>
<td>0.009</td>
</tr>
<tr>
<td>Li (7)</td>
<td>6.58</td>
<td>6.15</td>
<td>93</td>
<td>8</td>
<td>0.184</td>
</tr>
<tr>
<td>Mo (95)</td>
<td>2.4</td>
<td>1.95</td>
<td>81</td>
<td>13</td>
<td>0.005</td>
</tr>
<tr>
<td>Nb (93)</td>
<td>6.8</td>
<td>5.53</td>
<td>81</td>
<td>7</td>
<td>0.014</td>
</tr>
<tr>
<td>Ni (60)</td>
<td>454</td>
<td>428</td>
<td>94</td>
<td>9</td>
<td>0.145</td>
</tr>
<tr>
<td>Pb (207)</td>
<td>18.2</td>
<td>22</td>
<td>121</td>
<td>11</td>
<td>0.021</td>
</tr>
<tr>
<td>Pd (105)</td>
<td>0.066</td>
<td>0.065</td>
<td>99</td>
<td>4</td>
<td>0.01</td>
</tr>
<tr>
<td>Pt (195)</td>
<td>0.108</td>
<td>0.112</td>
<td>104</td>
<td>6</td>
<td>0.004</td>
</tr>
<tr>
<td>Rb (85)</td>
<td>21.2</td>
<td>21.01</td>
<td>99</td>
<td>6</td>
<td>0.006</td>
</tr>
<tr>
<td>Sb (121)</td>
<td>1</td>
<td>1.06</td>
<td>106</td>
<td>8</td>
<td>0.01</td>
</tr>
<tr>
<td>Sc (45)</td>
<td>93</td>
<td>94.7</td>
<td>102</td>
<td>7</td>
<td>0.052</td>
</tr>
<tr>
<td>Sn (118)</td>
<td>1.32</td>
<td>1.48</td>
<td>112</td>
<td>9</td>
<td>0.028</td>
</tr>
<tr>
<td>Sr (86)</td>
<td>15.9</td>
<td>14.2</td>
<td>89</td>
<td>7</td>
<td>0.087</td>
</tr>
</tbody>
</table>
Table 3: Statistical evaluation of results obtained using various preparation procedures and various techniques for OREAS 45f soil CRM

<table>
<thead>
<tr>
<th>Element</th>
<th>Certified value, mg/kg</th>
<th>Measured average (n = 20), mg/kg</th>
<th>Recovery, %</th>
<th>RSD, %</th>
<th>LOD, ng/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (107)</td>
<td>0.057</td>
<td>0.061</td>
<td>107</td>
<td>7</td>
<td>0.01</td>
</tr>
<tr>
<td>Au (197)</td>
<td>0.018</td>
<td>0.0184</td>
<td>102</td>
<td>5</td>
<td>0.002</td>
</tr>
<tr>
<td>As (75)</td>
<td>9.67</td>
<td>7.80</td>
<td>81</td>
<td>10</td>
<td>0.069</td>
</tr>
<tr>
<td>Ba (136)</td>
<td>206</td>
<td>214</td>
<td>104</td>
<td>4</td>
<td>0.043</td>
</tr>
<tr>
<td>Be (9)</td>
<td>1.2</td>
<td>0.97</td>
<td>81</td>
<td>9</td>
<td>0.01</td>
</tr>
<tr>
<td>Bi (209)</td>
<td>0.21</td>
<td>0.21</td>
<td>100</td>
<td>3</td>
<td>0.005</td>
</tr>
<tr>
<td>Ce (140)</td>
<td>28.8</td>
<td>23.1</td>
<td>80</td>
<td>9</td>
<td>0.04</td>
</tr>
<tr>
<td>Co (59)</td>
<td>44.5</td>
<td>44.1</td>
<td>99</td>
<td>7</td>
<td>0.085</td>
</tr>
<tr>
<td>Cs (133)</td>
<td>3.65</td>
<td>3.35</td>
<td>92</td>
<td>8</td>
<td>0.123</td>
</tr>
<tr>
<td>Cu (63)</td>
<td>363</td>
<td>329</td>
<td>91</td>
<td>9</td>
<td>0.005</td>
</tr>
<tr>
<td>Ga (69)</td>
<td>26.7</td>
<td>25.3</td>
<td>95</td>
<td>4</td>
<td>0.002</td>
</tr>
<tr>
<td>Hf (178)</td>
<td>4.64</td>
<td>3.92</td>
<td>84</td>
<td>6</td>
<td>0.001</td>
</tr>
<tr>
<td>In (115)</td>
<td>0.11</td>
<td>0.10</td>
<td>93</td>
<td>6</td>
<td>0.005</td>
</tr>
<tr>
<td>La (139)</td>
<td>15.7</td>
<td>16.2</td>
<td>103</td>
<td>5</td>
<td>0.009</td>
</tr>
<tr>
<td>Li (7)</td>
<td>20.4</td>
<td>19.1</td>
<td>93</td>
<td>9</td>
<td>0.184</td>
</tr>
<tr>
<td>Mo (95)</td>
<td>2.27</td>
<td>1.81</td>
<td>80</td>
<td>11</td>
<td>0.005</td>
</tr>
<tr>
<td>Nb (93)</td>
<td>23.1</td>
<td>19.7</td>
<td>85</td>
<td>8</td>
<td>0.014</td>
</tr>
<tr>
<td>Ni (60)</td>
<td>256</td>
<td>236</td>
<td>92</td>
<td>8</td>
<td>0.145</td>
</tr>
<tr>
<td>Pb (207)</td>
<td>14.7</td>
<td>15.2</td>
<td>103</td>
<td>7</td>
<td>0.021</td>
</tr>
<tr>
<td>Pd (105)</td>
<td>0.0399</td>
<td>0.0396</td>
<td>99</td>
<td>15</td>
<td>0.01</td>
</tr>
<tr>
<td>Pt (195)</td>
<td>0.0367</td>
<td>0.04</td>
<td>107</td>
<td>7</td>
<td>0.004</td>
</tr>
<tr>
<td>Rb (85)</td>
<td>31.2</td>
<td>28.2</td>
<td>90</td>
<td>4</td>
<td>0.006</td>
</tr>
<tr>
<td>Sb (121)</td>
<td>0.64</td>
<td>0.72</td>
<td>113</td>
<td>9</td>
<td>0.01</td>
</tr>
<tr>
<td>Sc (45)</td>
<td>36.3</td>
<td>32.5</td>
<td>90</td>
<td>8</td>
<td>0.052</td>
</tr>
<tr>
<td>Sn (118)</td>
<td>2.85</td>
<td>2.83</td>
<td>99</td>
<td>5</td>
<td>0.028</td>
</tr>
<tr>
<td>Sr (86)</td>
<td>25.1</td>
<td>28.28</td>
<td>113</td>
<td>13</td>
<td>0.087</td>
</tr>
<tr>
<td>Ta (181)</td>
<td>1.66</td>
<td>1.82</td>
<td>109</td>
<td>8</td>
<td>0.008</td>
</tr>
<tr>
<td>Th (232)</td>
<td>9.99</td>
<td>10.97</td>
<td>110</td>
<td>5</td>
<td>0.026</td>
</tr>
<tr>
<td>Tl (205)</td>
<td>0.2</td>
<td>0.16</td>
<td>80</td>
<td>5</td>
<td>0.002</td>
</tr>
<tr>
<td>U (238)</td>
<td>2.09</td>
<td>2.03</td>
<td>97</td>
<td>7</td>
<td>0.002</td>
</tr>
<tr>
<td>V (51)</td>
<td>253</td>
<td>236</td>
<td>93</td>
<td>9</td>
<td>0.08</td>
</tr>
<tr>
<td>W (184)</td>
<td>1.27</td>
<td>1.31</td>
<td>103</td>
<td>6</td>
<td>0.001</td>
</tr>
</tbody>
</table>
The instrument detection limit (IDL) was calculated from the mean of replicate analysis \((n = 10)\) of total method blank solutions plus 3s (confidence level of about 90%) [7]. The ICP-MS technique yielded recoveries between 80 to 113% for major and most trace elements and good repeatability (low RSDs). Most elements were quantitatively extracted with 4-acid digestion and PGMs were successfully extracted with aqua regia digestion. Good recoveries on PGMs and Ag were obtained when the analyses done on KED mode (improved sensitivity) compared to STD mode. There were also challenges with instrumental drift due to sample introduction problems (clogging of the cone orifice) caused by total dissolved solids (TDS) as 10g of sample was digested into 200 ml.

The method could be improved by using two internal standards, a suitable low mass element to be used as an internal standard for the elements in the low mass range, for example, Ga or In provided they are low in concentration and may not mask the natural occurrence.

![Figure 1: Example of repeatability graph showing average daily hafnium and thorium values in OREAS 45e soil CRM](image)

All batches were analysed with quality control solutions and repeated should the data fell outside accepted limits. To monitor instrument performance and method repeatability, few elements were selected and analysed for twelve consecutive days and plotted, an example is shown in figure 1 for OREAS 45e.

**3.2 Evaluation of analytical data on real samples**

Real geological (soil) samples were then analyzed in the same manner as certified materials, recommended preparation methods and analytical techniques at preferred wavelengths and isotopes. These samples were sent to an outside laboratory for confirmation of the results.
Traverse graphs of all elements analyzed were plotted against the data from Mintek (min) and the other laboratory (gen). Examples of some of the selected elements are shown in figures 2 to 4. Generally, good correlation was obtained for most major and trace elements.

Figure 2: Graph of U plotted on traverse against U-gen and U-min

Figure 3: Graph of Li plotted on traverse against Li-gen and Li-min
4 Conclusion

Analysis of the geological samples by ICP-MS was successful. In order to get best possible applicable digestion methods and analytical techniques for analysis of soil samples, two soil international certified reference materials (CRMs) from OREAS namely, OREAS 45e and OREAS 45f were used to develop a method that can be employed in analyzing real soil samples for geochemical mapping. After exploring suitable methods, twenty-nine elements were quantitatively extracted using the multi-acid digestion and aqua regia digestion (for Ag, Au, Pd and Pt) and analyzed by ICP-MS. Good recoveries (80 to 113%) for most major and trace elements were obtained, even though some elements had low recoveries (e.g., Be and Nb) the repeatability was good (RSD < 10%), and therefore these data could still be used to produce relevant geochemical maps.

The method could be improved by using two internal standards, a suitable low mass element to be used as an internal standard for the elements in the low mass range, as Ir (193) that was used in this exercise only corrects for elements with high mass. Results for real sample gave good correlation when compared with results from an external laboratory.

References


