Determination of sodium and potassium in certified rock samples by AES after ultrasonic leaching

MEHMET HIKMET ÖZKAN, AYSUN ÖZKAN, RAMAZAN GÜRKAN* and MEHMED AKÇAY

University of Cumhuriyet, Faculty of Science and Arts, Department of Chemistry, 58140, Sivas, Turkey (e-mail: rgurkan@cumhuriyet.edu.tr)

(Received 19 May, revised 27 December 2005)

Abstract: In order to evaluate the data obtained by atomic emission spectrometric analysis after ultrasonic extraction, destructive analysis of some certified rock samples employing ultrasonic waves was applied to two elements, Na and K, and the recovery rates were defined. The recovery ratio as $K_1 = \frac{C_{ULM}}{C_{CRM}}$ was defined for the ultrasonic leaching method ($C_{ULM}$) and the certified reference materials (CRMs). Another recovery ratio, $K_2$ was also defined from the results of the conventional dissolution method ($C_{CDM}$), that is $K_2 = \frac{C_{ULM}}{C_{CDM}}$. The accuracy and precision of the method were comparable with those of the conventional methods. The obtained recoveries were between 90.0 % < $K_1$, Na < 106.1 and 90.0 % < $K_2$, Na < 103.0 % for Na and 92.3 % < $K_1$, K < 103.2 and 92.3 % < $K_2$, K < 104.5 % for K. It was shown that ultrasonic extraction can be effectively used for analytical sample preparation purposes.

Keywords: ultrasonic metal leaching, partial leaching, rocks, and flame–AES.

INTRODUCTION

The sample preparation step is frequently very time-consuming and a major potential source of error in any geochemical analysis. In addition, there is excess acid consumption in conventional sample preparation techniques.1–6 Despite advances in instrumentation and microcomputer technology, many sample preparation practices are based on nineteenth-century technologies. Furthermore, there is a serious contamination risk with these procedures. An ideal dissolution technique should be economical, simple, effective, and selective (for possible interference problems) and require minimum solvent usage.7

Grained rock samples can be leached in a reproducible manner for analytical purposes.

One of the techniques, which appears promising for accelerating and simplifying sample treatment is ultrasonic extraction. Furthermore, once an analyte is dis-
solved, ultrasonic waves should prevent its deposition onto solid residue and adsorption onto a solid surface. Ultrasonic energy, when imparted to solutions, causes acoustic cavitations, that is, bubble formation and subsequent implosion. The collapse of the bubbles created by the sonication of solutions results in the generation of extremely high local temperature and pressure gradients, which may be regarded as localized hot spots. On a timescale of about $10^5$ s, effective local pressures and energies of about $10^{10}$ Pa and about 1 eV, respectively, are generated under sonochemical conditions. These localized high energy environments formed by the application of ultrasound to suspensions of solvent and sample can be employed for the purpose of extracting elemental analytes from solid matrices. When the speed of the procedure, as well as the reproducibility and solvent consumption are considered, ultrasonic leaching has some advantages, such as speed and reproducibility, over traditional methods. The ultrasonic leaching method (ULM) is considered to be an alternative method to conventional total dissolution techniques. Optimization of the conditions, such as ultrasonication times, ultrasonic power, the nature of sample, sample weight, particle size, and extraction media, should be studied on the samples for high recovery of elements from inorganic matrices by ultrasonication.

The time is also important for total analyte extraction by ultrasonic waves, which depends on the sample matrices. In general, ultrasonication times for high recovery of elements is varied for biological samples (5–10 min), human hair (10 min), plants (10–20 min), sediments (30 min), atmospheric particulate (10–20 min), geological samples (30 min), and heavy metals in bio-collectors (20 min).

In this study, the Na and K recovery ratios in certified rock samples were investigated by AES after ultrasonic extraction. The obtained results were compared with those of a conventional method, and the recovery ratios, $K_1$ and $K_2$, were determined.

**EXPERIMENTAL**

*Certified Reference Rock Samples (CRM)*

Values of elemental concentrations of CR were obtained from Govindaraju. The CRMs used in this study are as follows:

- CRPG: Centre de Recherches Petrographiques et Geochemiques, France.

Sample Preparation for the Analysis of CRMs

Two methods were used to prepare the samples.

A) Conventional Dissolution Method: The certified rock samples were dissolved employing a conventional total dissolution method.
B) Ultrasonic Leaching Method: As reported previously\textsuperscript{8,9,16} after an optimized softening procedure, which involves HF+H\textsubscript{2}O (2/2, v/v), the residue of the CRMs were leached under ultrasonic treatment as follows:

\textbf{Dissolution by ULM.} The residue after silica removal was placed in a 120 ml glass beaker, 25 ml of 1\% HCl (Merck, Darmstadt, Germany) was added and the beakers were kept in ultrasonic bath, NEY 300 model (at 40–50 kHz nominal frequency), for leaching. The leached solutions were centrifuged at 5000 rpm for 10 min to separate the residue and the supernatents were filtered using Whatman 41-filtration paper. 1 ml of 1\% La\textsuperscript{3+} (for improvement of the atomization efficiency in the AAS analysis and 1 ml of concentrated HCl were added to the samples which were made up to 50 ml with 1.0 \% HCl solution and kept in LDPE (low density polyethylene) bottle for analysis.\textsuperscript{7}

The optimum ULM dissolution was obtained when the ultrasonic time was 30 min the sample mass is 0.0500 g and the maximum USP was used for grain size 1.

\textbf{Determination of the elements}

The leaching solutions were analyzed for the determination of Na and K with a flame atomic emission spectrophotometer (FAES-UNICAM 929 model) using both the standard addition and calibration curve techniques. Different recovery studies were performet to check both the accuracy of the employed procedures and to test possible interferences. For this purpose, recovery studies based on the direct addition of known amounts of Na and K elements to pre-analyzed certified standard materials were performed by spiking into the extraction media, separately. Recoveries obtained from direct spiking of known amounts of the relevant elements (0.2 mg 1\textsuperscript{-1}) into the pre-analyzed certified standard materials (0.1 mg 1\textsuperscript{-1}) were found to be between 92–103 \% for Na and between 95–104 \% for K for the extraction procedures. The recovery varied depending on the nature of the certified standard material and the procedure applied. Based on these recovery results, it was assumed that there were no significant interference effects arising from the nature of the samples. Therefore, the calibration curve technique was used for the analyses. An air–acetylene flame was used for the determination of Na and K. For the analyses of the content of sodium and potassium in the certified standard reference materials, calibration curves were prepared using certified standard reference materials for the two elements.\textsuperscript{18} The method was based on the measurement of the direct emission intensities of metal solutions by means of AES. The equation of linear curves for Na and K were, respectiveles as follows:

\begin{align*}
I &= 160.99c\textsubscript{Na}+4.1115, \quad R^2 = 0.9980 \\
I &= 169.30c\textsubscript{K}+0.3736, \quad R^2 = 0.9994
\end{align*}

The calibration ranges were between 0.05–0.60 mg 1\textsuperscript{-1} for Na and K, respectively. In order to obtain the dynamic range of the calibration curves, all samples were diluted by a factor of 10, 50, or 100 with 1 \% HCl, prior to analysis. The concentrations of the elements were obtained as the mean of three readings, which provided less than 2 \% relative standard deviation (RSD \%).

\textbf{RESULTS AND DISCUSSION}

The effects of sonication time, sample mass, grain size and ultrasonic power on the ultrasonic leaching were studied.

\textit{The effect of sonication time on the solubility of sodium and potassium}

In this study, in order to determine the optimum sonication time for the samples analyzed, experiments were performed with various sonication times with the corresponding samples. Following these model experiments, an ultrasonication time of 60 min was determined for Na and K in the standard rock samples (SDC-1).
Fig. 1. The change in sodium and potassium levels with sonication time for SDC-1 standard rock sample (0.0500 g sample mass grain size 1 and maximum USP).

The change in solubilities of Na and K (for a 0.0500 g sample mass, grain size 1 and maximum USP) in dependence on the sonication time are shown in Fig. 1.

The sodium and potassium concentration in the sample increased with increasing sonication period in the first 30 minutes and then remained constant. Since the maximum Na and K concentration was achieved after 30 min, this was concluded to be the optimum sonication time for a 0.0500 g sample mass, grain size 1 and maximum USP.

The constant solubility of Na and K oxides at 30, 40, 50 and 60 min were used for reproducibility tests.

Evaluation of the solubilities of Na and K

Sodium and potassium are mainly present as Na$_2$O and K$_2$O in rock samples. These major elements as the main rock forming components in magmatic rocks are incorporated in the formation of feldspar and mafic minerals.\textsuperscript{20,21} It has been reported that a high recovery of oxide bound strontium from sediments is achieved when analyzed by sequential ULM in a shorter time than those of required for conventional sequential extraction procedures.\textsuperscript{22} Similar results have also been reported for oxide bound elements (Na, K, Ca, Mg, Al, Mn and Fe) in rock samples because of the physical and chemical effects of ultrasonication.\textsuperscript{8–10} In fact, under the optimized conditions, practically no residual remained after ULM. In other words, the results of this procedure are in agreement with those of the conventional destructive one. The CRMs were leached under the optimized ULM conditions and by the conventional method. All experiments were repeated four times. All the leachates were analyzed using AES, and results were defined for Na and K as an average percentage including recovery efficiency percentage as follows:
The CRMs used in this study and the \( K_1 \) and \( K_2 \) values are given Tables I and II.

### Table I. The sodium oxide, Na\(_2\)O % values of CRM and the recovery ratios

<table>
<thead>
<tr>
<th>SRM</th>
<th>( C_{\text{CRM}} )</th>
<th>( C^{a}_{\text{ULM}} )</th>
<th>( K_1 ) (( C_{\text{ULM}}^{a}/C_{\text{CRM}} ))^b</th>
<th>( C^c_{\text{CDM}} )</th>
<th>( K_2 ) (( C_{\text{ULM}}^{a}/C_{\text{CDM}} ))^d</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVG-1</td>
<td>4.26</td>
<td>4.09</td>
<td>96.0</td>
<td>4.31</td>
<td>94.9</td>
</tr>
<tr>
<td>G-2</td>
<td>4.08</td>
<td>3.96</td>
<td>97.1</td>
<td>4.07</td>
<td>97.3</td>
</tr>
<tr>
<td>RGM-1</td>
<td>4.07</td>
<td>4.19</td>
<td>102.3</td>
<td>4.15</td>
<td>100.9</td>
</tr>
<tr>
<td>SDC-1</td>
<td>2.05</td>
<td>2.07</td>
<td>101.0</td>
<td>2.22</td>
<td>93.2</td>
</tr>
<tr>
<td>GA</td>
<td>3.55</td>
<td>3.61</td>
<td>101.7</td>
<td>3.50</td>
<td>103.1</td>
</tr>
<tr>
<td>GH</td>
<td>3.85</td>
<td>3.67</td>
<td>95.3</td>
<td>3.75</td>
<td>97.9</td>
</tr>
<tr>
<td>Mica Fe</td>
<td>0.30</td>
<td>0.28</td>
<td>93.3</td>
<td>0.31</td>
<td>90.3</td>
</tr>
<tr>
<td>DRN</td>
<td>2.99</td>
<td>3.13</td>
<td>104.7</td>
<td>3.18</td>
<td>98.4</td>
</tr>
<tr>
<td>GSN</td>
<td>3.77</td>
<td>3.56</td>
<td>94.4</td>
<td>3.67</td>
<td>97.0</td>
</tr>
<tr>
<td>MA-N</td>
<td>5.84</td>
<td>5.68</td>
<td>97.3</td>
<td>5.78</td>
<td>98.3</td>
</tr>
<tr>
<td>AC-E</td>
<td>6.54</td>
<td>6.38</td>
<td>97.6</td>
<td>6.60</td>
<td>96.7</td>
</tr>
<tr>
<td>Mica–Mg</td>
<td>0.12</td>
<td>0.11</td>
<td>91.7</td>
<td>0.11</td>
<td>100.0</td>
</tr>
<tr>
<td>UBN</td>
<td>0.10</td>
<td>0.10</td>
<td>100.0</td>
<td>0.10</td>
<td>100.0</td>
</tr>
<tr>
<td>ANG</td>
<td>1.63</td>
<td>1.71</td>
<td>106.1</td>
<td>1.66</td>
<td>103.0</td>
</tr>
<tr>
<td>BEN</td>
<td>3.18</td>
<td>3.13</td>
<td>98.4</td>
<td>3.22</td>
<td>97.2</td>
</tr>
</tbody>
</table>

\( a) \) Pooled standard deviation (\( \sigma \)) = 0.045 for \( N = 60 \) and degree of freedom = 45; \( b) \) Percentage confidence interval = ±4.4 (\( P = 0.05 \) and \( N = 4 \)); \( c) \) Pooled standard deviation (\( \sigma \)) = 0.052 for \( N = 60 \) and degree of freedom = 45; \( d) \) Percentage confidence interval = ± 5.1 (\( P = 0.05 \) and \( N = 4 \))

### Table II. The potassium oxide, K\(_2\)O % values of CRM and the recovery ratios

<table>
<thead>
<tr>
<th>SRM</th>
<th>( C_{\text{CRM}} )</th>
<th>( C^{a}_{\text{ULM}} )</th>
<th>( K_1 ) (( C_{\text{ULM}}^{a}/C_{\text{CRM}} ))^b</th>
<th>( C^c_{\text{CDM}} )</th>
<th>( K_2 ) (( C_{\text{ULM}}^{a}/C_{\text{CDM}} ))^d</th>
</tr>
</thead>
<tbody>
<tr>
<td>AVG-1</td>
<td>2.91</td>
<td>2.82</td>
<td>96.9</td>
<td>2.85</td>
<td>98.9</td>
</tr>
<tr>
<td>G-2</td>
<td>4.48</td>
<td>4.32</td>
<td>96.4</td>
<td>4.57</td>
<td>94.5</td>
</tr>
<tr>
<td>RGM-1</td>
<td>4.30</td>
<td>4.12</td>
<td>95.8</td>
<td>4.41</td>
<td>93.4</td>
</tr>
<tr>
<td>SCD-1</td>
<td>3.28</td>
<td>3.20</td>
<td>97.6</td>
<td>3.11</td>
<td>102.9</td>
</tr>
<tr>
<td>GA</td>
<td>4.03</td>
<td>4.16</td>
<td>103.2</td>
<td>4.10</td>
<td>101.5</td>
</tr>
<tr>
<td>GH</td>
<td>4.76</td>
<td>4.57</td>
<td>96.0</td>
<td>4.93</td>
<td>92.7</td>
</tr>
<tr>
<td>Mica–Fe</td>
<td>8.75</td>
<td>8.58</td>
<td>98.1</td>
<td>8.42</td>
<td>101.9</td>
</tr>
<tr>
<td>DRN</td>
<td>1.70</td>
<td>1.61</td>
<td>94.5</td>
<td>1.73</td>
<td>93.1</td>
</tr>
<tr>
<td>GSN</td>
<td>4.63</td>
<td>4.53</td>
<td>97.8</td>
<td>4.75</td>
<td>95.4</td>
</tr>
<tr>
<td>MA-N</td>
<td>3.18</td>
<td>3.25</td>
<td>102.2</td>
<td>3.11</td>
<td>104.5</td>
</tr>
<tr>
<td>AC-E</td>
<td>4.49</td>
<td>4.42</td>
<td>98.4</td>
<td>4.58</td>
<td>96.5</td>
</tr>
<tr>
<td>Mica–Mg</td>
<td>10.00</td>
<td>9.78</td>
<td>97.8</td>
<td>9.61</td>
<td>101.8</td>
</tr>
</tbody>
</table>
When the concentrations of Na and K obtained by ULM under optimized conditions are compared with those of the conventional method, there was no significant difference between the results.23 The percent recovery was in the range 93.3 – 106.1 for Na and 92.3 – 104.5 for K.

CONCLUSIONS

The utilization of ultrasonic extraction for the determination of sodium and potassium in rock sample by atomic spectrometry has been demonstrated. A strategy employing ultrasonic extraction for sample preparation has been presented. Several benefits offered by ultrasonic extraction are: shortened sample preparation times, simplicity, and enhanced safety compared to other more traditional methods of preparing samples for subsequent elemental determination. Another advantage of ultrasonic extraction is that there is no possibility of the extraction solution evaporating to dryness. This is often a problem with hot plate digestion, especially when such digestions are carried out in low solution volumes. The ULM results were compared with the results determined by CDM in certified reference rock materials and there were no significant differences for ULM and CDM at the 95 % confidence level for \( n = 4 \). Reproducible element recovery ratios were obtained under well-defined partial dissolution conditions. Similar results were obtained for the investigated elements. Hence, of seems that the situation does not depend on the nature of the element. The confidence interval of the method is comparable with those of conventional techniques. The reactive consumption of the method is less than those of the total dissolution, and a shorter dissolution time (ten times faster than CDM) was required.

Less reactive chemicals and less energy are required and the analyst is also exposed to less toxic gases. It is clear that the ULM is a rapid, easy, reproducible and selective technique for the determination Na and K in rock materials. As a result, it can be concluded that ultrasonic extraction might be further used for analytical purposes in future owing to its simplicity, speed, safety and performance of this sample preparation technique.

Acknowledgements: The authors wish to express their gratitude to the University of Cumhuriyet, Faculty of Science and Arts, Department of Chemistry for Experimental Studies. The authors are also very grateful to Dr. M. Sökmen at the Department of Chemistry for her valuable assistance.
IZVOD
ODREĐIVANJE NATRIJUMA I KALIJUMA U SERTIFIKOVANIM UZORCIMA STENA ATOMSKOM EMISIONOM SPEKTROSKOPIJOM POSLE ULTRAZVUČNE EKSTRAKCIJE
MEHMET HİKMET ÖZKAN, AYSUN ÖZKAN, RAMAZAN GÜRKAN i MEHMET AKÇAY
University of Cumhuriyet, Faculty of Science and Arts, Department of Chemistry, 58140, Sivas, Turkey

U cilju evaluacije podataka dobijenih atomskom emisionom spektrometrijskom analizom posle ultrazvučne ekstrakcije (CULM) izvedeno je određivanje natrijuma i kalijuma u sertifikovanim uzorcima stena. Izračunati su odnosi prinosa iz dobijenih vrednosti posle ultrazvučne ekstrakcije i dati za sertifikovane referentne materijale (CRM), kao $K_{1}=C_{ULM}/C_{CRM}$. Izračunati su takođe i odnosi prinosa sa rezultatima dobijenim konvencionalnom metodom pripreme uzorka $K_{2}$, kao $C_{ULM}/C_{CRM}$. Tačnost i preciznost metode, koja uključuje ultrazvučnu ekstrakciju je porediva sa konvencionalnom metodom. Dobijene vrednosti prinosa su u opsegu: $90,0\% < K_{1,Na} < 106,1\%$ i $92,3\% < K_{1,K} < 103,2\%$ za Na i $92,3\% < K_{1,K} < 104,5\%$ za K. Dobijeni rezultati ukazuju da se ultrazvučna ekstrakcija može uspešno koristiti u analitičke svrhe u analizi uzoraka stena.

(Primenjeno 19. maj, revizionato 27. decembra 2005)

REFERENCES