Determination of Uranium in Phosphate Rocks by Fusion Glass Method for X-Ray Fluorescence

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Abstract

A flux of lithium metaborate (2.20 g) and lithium tetraborate (1.20 g) was used to fuse oxides and salts in phosphate rocks. NaNO₃, 0.50 g, was added as an oxidizing agent, while, SiO₂, 0.1 g, was added for glassing at 700 °C for 10 min. Uranium in glass samples was determined by ED-XRF technique. The calibration curve was linear in a concentration range of 12 ppm - 827 ppm with a correlation coefficient, R², of 0.9980. The RSD (n=3) for uranium determined in NIST standard reference material was a value of ± 1.0 % at 370 ppm. The glass samples were used for the determination of U in phosphate rocks. The results of uranium determined by fusion glass method were in good agreement with those obtained by SQ-XRF, fluorometry and γ-ray methods.

Ca, Sr and Fe elements were also determined with the developed fusion glass method. The results of these elements were comparable to those obtained by AAS.

Keywords: XRF, fusion glass, lithium metaborate, lithium tetraborate, calibration curve

Introduction

Generally, x-ray fluorescence analysis deals with solid and homogeneous samples. Particle size of the sample affects x-ray incident with wavelength > 3 Å. Fusion glass technique is the approach, which is mostly used for solving a homogeneity problem and matrix effect.

Fusion glass procedure includes heating the sample, which is mixed with a suitable flux, at a relatively high temperature for a limited period of time. The heavy absorber may be proposed for decreasing the matrix effect. The prepared glass samples are usually used as standard reference samples, due to their stability throughout the time of multiplication and analysis. Unfortunately, the fusion glass approach is time-consuming and a sample is subjected for dilution.

Different reagents are recommended for the use as suitable fluxes for different matrices [1-4]. The flux is chosen according to the composition and physical and chemical properties of the sample. For example, potassium pyrosulphate is used for the
fusion of samples at low temperature [5]. A lithium meta- and tetra- borate or a sodium tetraborate are often used as fluxes [6, 7]. Fusion with lithium borate salts is usually preferred due to the relatively low viscosity of the melt; consequently low tendency of sticking with the crucible [8-10]. Many workers use the ratio of flux-to-sample in the range of 1:1-10:1 [11]. In addition, lithium metaborate is widely used due to its ability to dissolve many matrices with no requirements for a large number of dilutions of the sample [8]. Although the use of mathematical approach solves the enter-element effect, which is raised from preparing glass samples with a small ratio of flux-to-sample [12], the practical approach is still in use for the analysis of different matrices. However, borate salts are usually employed for fusion of silicates, alloys, plant materials, metals and soils [1-4, 13, 14]. Studies on lithium borate fluxes have not dealt yet with the determination of uranium in phosphate rocks using fusion method for XRF.

This work focuses on: (i) the determination of uranium in phosphate rocks using a mixture of lithium meta- and tetra- borate with a pre-oxidation of the sample by sodium nitrate; (ii) determination of some other elements, e.g. Ca, Sr and Fe in the same samples; (iii) evaluation of the precision and accuracy of the developed fusion glass method for XRF analysis.

Experimental
a. Apparatus and instrumental conditions

X-ray fluorescence (XRF) determinations were performed using a Si(Li) detector with an active area of 30 mm², FWHM ~ 180 eV at 5.9 keV and a PCAII multi-channel analyzer. X-ray tube with a secondary target of Mo was used with operation conditions of 50 mA and 45 kV. Net intensity was measured using the AXIL program, which was developed in the IAEN laboratories [15]. γ-ray spectrometer equipped with a HPGe detector (eff. 12.5 %, FWHM = 0.998 keV at 122 keV and 1.88 keV at 1332 keV) and a fluorometer (GMBH-G-M fluorometer, Jereell-Ash-27000) were also used for the determination of uranium in phosphate rocks. Ca, Sr and Fe elements were determined by a Perkin-Elmer 2380 atomic absorption spectrophotometer.

All reagents used in this study were of analytical-reagent grade.

b. Preparation of glass samples

Glass samples were prepared as mentioned elsewhere [8]. 22 and 12 parts of lithium metaborate and lithium tetraborate (weight of the mixture was 3.40 g), respectively, were mixed thoroughly in a crucible made of Pt 95 % - Au 5 %. The mixture was heated at 280 °C for two hours. An amount of 0.33 g of a sample was added to the dry flux. Pre-oxidation of the sample was attended using 0.5 g of NaNO₃. A small amount (0.1 g) of NH₄Cl was added as a releasing agent; 0.27 g of SiO₂ was added for a glassing.

The mixture was then heated in electrical furnace at 700 °C for 10 min; after which fusion of the sample was carried out at 1000 °C for 10 min. The melt was subjected to a rapid cooling in a Pt 95 % - Au 5 % dish. Finally, the sample was kept in desiccators for further XRF measurements.
However, the preparation of glass samples was consisted of the following steps:

1. Pre-oxidation of the samples with NaNO₃ at 700 °C for 10 min.
2. Addition of a releasing agent, i.e. NH₄Cl, to prevent sticking of the melt in the bottom of the crucible and SiO₂ to prepare glass samples free of cracking.
3. Fusion of the samples at 1000 °C for 10 min.
4. Rapid cooling of the melts at ambient temperature.
5. Keeping the glass samples in desiccators for further work.

c. Calibration curve

The calibration curve, representing the relation between the intensity (cps) of XRF and the concentration of U (ppm), was constructed using a series of synthetic glass samples. The concentrations of U in synthetic samples, 12-827 ppm, covered the range of this element in phosphate rocks. Other compounds, e.g. P₂O₅, CaO, Al₂O₃, NaF, Na₂O, MgO, KH₂PO₄, SrO, ZrO₂, Y₂O₃ were added to the synthetic samples to match the content of elements in the unknown ones.

d. Phosphate soils analysis

Four phosphate soil samples were collected from the Sharkeih and Khneifes phosphate mines, which are located in eastern side of Palmyra in the middle of Syria. The samples were ground to fine particles and homogenized for further analyses. The samples were fused in a similar way described for the standard samples. The samples were analyzed by fusion glass technique for XRF using the previously mentioned calibration curve method. The results were compared with those obtained using γ-ray, fluorometry, and simple quantitative and fundamental parameter methods for XRF.

Results and discussion

The experiment showed that pre-heating of the 22:12 mixture at 280 °C for 2 hours is preferable to avoid the swelling of flux granules. The free from crack and homogenous synthetic glass samples were subjected for analysis by XRF technique. The net intensity (count per seconds=cps) of U (Lα= 13.6 keV) in these samples was determined using AXIL program. Figure 1 shows a linear relationship between the net intensity, I₀, and the concentration of U (C₀). The computed concentration of uranium was calculated using the following equation: I₀ = f (C₀). Linearity of the calibration curve was obtained by plotting computed U concentration against used U concentration (Figure 2). The later Figure shows a good linearity represented by a correlation coefficient (R²) of 0.9980.
Fig. 1. Calibration curve of uranium

Fig. 2. The relationship between the computed and chemical concentrations of U in synthetic fusion glass samples

The lowest limit of uranium concentration (LLC) was calculated using the following equation: LLC = (2m)(Ib/Tb)² [11]; where: m is the sensitivity given as cps/ppm; Ib is the intensity of the background (cps); Tb is time of measurement. By applying the previously mentioned equation, the LLC of uranium was found to be 11 ppm, taking into account that m, 0.1343 cps/ppm, was obtained from the slope of the calibration curve (Fig. 1) and Ib, 0.546 cps, from measuring the counts at Lα = 13.6 keV for U in synthetic blank sample.
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The calibration curve method was applied for the determination of uranium in the phosphate uranium ore IAEA/S-17 standard reference material, which contains 370 ppm of uranium. The obtained mean value was 367.5 ppm with standard deviation (SD) of ±3.7 ppm. This indicates precision of 1.0 % for U determination using a fusion glass sample for XRF analysis; taking into account, the precision is represented by a standard relative error \( (\text{SRE}=(\text{SD}/C_{\text{av}}) \times 100, \%) \) at a probability level of 95 % and a number of measurements \( (n) \) equal to 3. The method was associated with an accuracy value of –0.70 %.

The determination of uranium concentration in phosphate rock samples, collected from Sharkel and Kneifor phosphate mines was carried out using the developed fusion glass sample for XRF. The results of later method were compared to those obtained by γ-ray spectrometry, fluorometry, and simple quantitative and fundamental parameter for XRF (Table 1). The results in this work were calculated using SD = ±1σ and n=3.

Precision value of uranium determination by the developed fusion glass method for XRF, ±2.5 %, was comparable to those resulted using standard methods, simple quantitative for XRF, ±2.8 %, γ-ray spectrometry, ±4.3 %, and fluorometry, ±6.0 % (Table 1). The precision obtained via fundamental parameter method for XRF was not of a good satisfaction, ±14.4 %.

In terms of accuracy, there was an agreement between the values of uranium determined by fusion glass method for XRF and those obtained by γ-ray, fluorometry and simple quantitative for XRF in order of values ≤ 7.9 % for 11 cases out from 12, suggesting the goodness of the proposed fusion glass method. The large variation occurred between fundamental parameter method for XRF and other methods were obtained, reflecting the presence of systematic error in the determination of uranium using fundamental parameter method for XRF.

Table 1. Uranium determination in phosphate rocks using different methods.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( ^{\gamma}\text{-SM} (n=3) )</th>
<th>( ^{\gamma}\text{FM} (n=3) )</th>
<th>( ^{\gamma}\text{SQM} )</th>
<th>( ^{\gamma}\text{FPM} )</th>
<th>( ^{\gamma}\text{FQM} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>96.4±3.3</td>
<td>95.4±5.3</td>
<td>97.3±2.1</td>
<td>81.3±3.5</td>
<td>101.5±1.7</td>
</tr>
<tr>
<td>A.Tina-3</td>
<td>68.7±2.2</td>
<td>74.0±1.0</td>
<td>78.7±3.8</td>
<td>71.0±2.6</td>
<td>73.1±2.9</td>
</tr>
<tr>
<td>A.Tina-5</td>
<td>63.4±2.0</td>
<td>58.0±1.0</td>
<td>71.0±2.7</td>
<td>58.9±5.8</td>
<td>66.4±1.0</td>
</tr>
<tr>
<td>Sch-21</td>
<td>41.5±1.8</td>
<td>40.0±2.4</td>
<td>41.7±0.8</td>
<td>36.8±5.3</td>
<td>42.0±1.9</td>
</tr>
</tbody>
</table>

Where: \( ^{\gamma} \) is the γ-ray spectroscopy method, \( ^{\gamma} \) is the fluorometry method, \( ^{\gamma}, ^{\gamma}, ^{\gamma}, ^{\gamma} \) are the simple quantitative, fundamental parameter and fusion glass methods for XRF, respectively.

It could be deduced that fusion glass method for XRF over performed other methods for the determination of uranium in phosphate rocks, as no correction factors were involved neither complicated mathematical approaches. In addition, the developed
fusion glass method showed the ability for multi-element determinations. Table 2 displays the results of the determination of Fe, Sr and Ca elements in the glass-prepared samples. Similar calibration curves were constructed to those obtained for uranium determination.

Table 2. Comparison between fusion glass method for XRF (FGM-XRF) and atomic absorption spectrophotometric (AAS) method for Fe, Sr and Ca determination in phosphate rocks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca (%o) AAS</th>
<th>Ca (%o) FGM</th>
<th>Sr (ppm) AAS</th>
<th>Sr (ppm) FGM</th>
<th>Fe (ppm) AAS</th>
<th>Fe (ppm) FGM</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>35.9±0.9</td>
<td>34.9±0.4</td>
<td>1591±40</td>
<td>1621±18</td>
<td>1097±28</td>
<td>832±107</td>
</tr>
<tr>
<td>A.Tin-3</td>
<td>35.9±1.2</td>
<td>37.6±0.2</td>
<td>1127±90</td>
<td>1148±22</td>
<td>458±151</td>
<td>535±118</td>
</tr>
<tr>
<td>A.Tin-5</td>
<td>36.2±1.6</td>
<td>37.5±0.9</td>
<td>1417±132</td>
<td>1249±27</td>
<td>453±151</td>
<td>407±190</td>
</tr>
<tr>
<td>Sdr-21</td>
<td>29.6±0.8</td>
<td>29.8±0.5</td>
<td>1307±150</td>
<td>1072±99</td>
<td>761±23</td>
<td>&lt;780</td>
</tr>
</tbody>
</table>

Conclusions

The results show the useful application of the 22:12 mixture flux of lithium meta-tetra borate for the fusion of phosphate rocks. The prepared synthetic samples were used for U determination with a satisfied precision and accuracy. The application of FGM was extended to determine Fe, Sr and Ca in the phosphate samples, recommending however the method for the multi-element determination using the calibration curve as a simple approach for analysis.

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تحديد نسبة اليورانيوم في صخور الفوسفات بطريقة الزجاج المنصرور بالأشعة السينية

علي خضر و محمد مروف

ملخص

استخدم مصروف مكون من ليقوق منبنا اليورانيوم (2.20 g) و ليقوق نترات اليورانيوم (1.20 g) لصوم الألكايد والأملاح في الصخور الفلسفاتية. أضيف 0.5 g من NaNO₃ ككمامolem. بينما أضيف 0.1 g من راين.docx من أجل التزجيج بالدرجة C 700 و لمدة 10 دقائق. عين اليورانيوم في العينات الزجاجية وقلنية التحليل بالأشعة السينية. كان منحنى المعابرية خطيًا في مجال من 827 ppm إلى 12 ppm 827 ppm قدراً من 0.9980. كان النطاق المعزيلي النقي 12 ppm. عمومًا، نتائج RSD مقابل كوارد قياس 3-n لتعيين اليورانيوم في العينة المعزيلة S17 % مسيرةً ± 1.0 % مقابل RSD التركيز 370 ppm. استخدمت العينات الزجاجية لتعيين اليورانيوم في الصخور الفلسفاتية. كانت نتائج تعيين اليورانيوم بطريقة الزجاج المنصرور على توافق جيد مع تلك النتائج التي تم الحصول عليها بطرق الفحل السبيسي بالأشعة السينية SQ-XRF و الفلوروميترية بالأشعة السينية SQ-XRF.

التحليل الوراثي لعينات Fe و Sr و Ca يمكن أيضاً العناصر Fe و Sr و Ca بطرق الزجاج المنصرور المطرزة و التي تم الحصول عليها بالتقنية الارتباط الأيوني AAS.

References

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