



A comparison of analytical methods for determining uranium and thorium in ores and mill tailings



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ABSTRACT

Three different methods for determining uranium and four for determining thorium in an apatite ore, black schist and mill tailings are compared. The aim of the comparative study is to obtain analytical verification of field results so that site characterization could be optimized without compromising reliability of the analysis. The samples were collected from a former pilot scale phosphate mine in Sokli, northern Finland and the Talvivaara nickel mine in Eastern Finland. A non-destructive, portable X-ray fluorescence (XRF) spectrometer was used on site to measure, semi-quantitatively, the composition of major elements, including thorium in each material. The samples were then analyzed by X-ray diffraction (XRD) to identify the main mineral components and electron probe micro-analysis (EPMA) used to identify the uranium and thorium-bearing minerals. Gamma spectrometry was used for direct determination of uranium and thorium isotopes in powdered samples. Thereafter, sample digestion experiments were performed with various acids to optimize the method for microwave digestion allowing determination of uranium and thorium by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and alpha spectrometry. For the latter method, uranium and thorium were separated using anion exchange resin filled in a column. The results show that overall a sample mass of 0.1–0.5 g with addition of 20 mL concentrated nitric acid is the most efficient means for extracting uranium and thorium simultaneously from apatite ore, black schist and mill tailings. The results for uranium and thorium concentrations determined by gamma spectrometry, alpha spectrometry and ICP-MS were in good agreement. Also the on-site measurements with portable XRF gave comparable results to other methods used in this study for thorium even without prior sample preparation.

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1. Introduction

There is increasing awareness of the radiological impact of industries that release naturally occurring radioactive material (NORM) to the environment. This material consists of parent nuclides ²³⁸U, ²³⁵U and ²³²Th along with their progeny in the respective decay series, including the highly radiotoxic nuclides ²²⁶Ra, ²¹⁰Pb and ²¹⁰Po. In order to assess the environmental impact of the radionuclides released, site characterization usually requires a large number of samples. Because of this, while accuracy and precision are vital, the practicality of processing sets limits on the viability of many methods.

The most commonly used techniques for the determination of uranium and thorium plus progeny are gamma and alpha spectrometry, which offer sufficiently low limits of detection typically ranging from few Bq with lab based HPGe to mBq for uranium and Bq for thorium

with lab based alpha spectrometry (Morrison and Murphy, 2006). The characteristic low values of minimum detectable activity and the possibility of obtaining isotopic information make alpha spectrometry a very suitable technique to determine the activity concentrations of radionuclides in environmental samples (Lozano et al., 2012). Environmental samples are routinely measured using gamma-ray spectrometry, some of its assets being ease of sample preparation, reasonable accuracy, comprehensive data for many radionuclides in one analysis and the possibility of determining isotopic disequilibrium in the natural decay chains of interest simultaneously (Hult et al., 2012; Oddone et al., 2008). However, developments in mass spectrometry have meant that this technique has gained in popularity for trace element analysis in recent years. The method is fast, precise, sensitive (typical limit of detection with lab based mass spectrometer is μ Bq for uranium and nBq for thorium Morrison and Murphy, 2006) and less laboratory preparation work is needed. On the other hand, analysis of low concentrations is more likely to be compromised by trace contaminants in labware and the reagents used. In addition, the determination of specific analytes suffers from interferences in the Inductively Coupled Plasma Mass Spectrometry

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technique. In modern quadrupole mass spectrometers these interferences can be minimized, but verification of analytical results still requires additional effort (Hou and Roos, 2008; Montaser and Golightly, 1992).

Alpha spectrometry and trace elemental analysis by ICP-MS require that the components of the solid samples are extracted into a solution phase that is suitable for these techniques. Therefore, complete digestion of samples must be ensured. For environmental samples, mineral acid digestion is considered to be sufficient, because the components that do not dissolve in strong mineral acids are generally not biologically or environmentally harmful. Non-oxidizing acids (HCl, HF, weak HClO₄ and weak H₂SO₄) dissolve metals with a reduction potential higher than that of hydrogen. If a non-oxidizing acid does not dissolve the material, an oxidizing acid is added (HNO₃, concentrated H₂SO₄ or concentrated HClO₄). Nitric acid is most commonly used in digestions. It is a very efficient oxidizing agent at concentrations > 2 M, as it also dissolves organic matter (Anon, 2000). Biotite, clay minerals and amorphous iron oxides dissolve for the most part, but many silicates and oxide minerals do not. Similarly, aqua regia does not dissolve most sparingly soluble silicates. Some elements can dissolve from the silicates but the silicate framework is mainly inert to aqua regia. HCl alone as a reducing acid does not oxidize organic matter (Anon, 2000; Koljonen, 1992). However, addition of HCl may play a critical role, for example in the avoidance of possible sudden increases in pressure during the digestion of organic-rich samples (Sun et al., 2001). Sulphuric acid has oxidizing properties, but a high boiling point (338 °C) sets limits to its efficient use. Consequently, sulphuric acid is not applicable in microwave digestion since the melting point of Teflon is 260 °C. HF is commonly used to dissolve silicates. It is added to the sample usually with another acid that has a higher boiling point (HNO₃ or HClO₄). If the sample is treated with HF in addition to aqua regia, most matrices can be dissolved and silicates dissolve for the most part (Montaser, 1998). Minerals that contain abundant aluminium and very sparingly soluble oxides, such as hematite and chromite, may not completely dissolve however (Koljonen, 1992). Further, use of HF may not be practical since it etches glassware and can damage the torch of an ICP-MS. Microwave digestion has become the standard method for acid digestions rather than traditional digestion in open beakers because it offers clear advantages: a shorter acid digestion time; better recovery of volatile elements and compounds; lower contamination levels; minimal volumes of reagents and more reproducible yield (Agazzi and Pirola, 2000).

The aim of this study is to find an efficient and reliable procedure for the determination of uranium and thorium in ores and mill tailings. First, a portable X-ray fluorescence (XRF) analyzer was used to obtain an estimate of uranium and thorium contents on site. Then, in the laboratory, the activity concentrations of uranium and thorium were measured using gamma spectrometry from solid samples. The mineral composition was determined by X-ray diffraction (XRD) and uranium and thorium-bearing minerals were identified by electron probe micro-analysis (EPMA). Thereafter, microwave digestion was performed with the most commonly used mineral acids, alone and in combination and at varying sample masses to determine uranium and thorium contents by ICP-MS and alpha spectrometry. This method optimization is part of an on-going project to study the mobilization of radionuclides and heavy metals from mining industries.

2. Materials and methods

2.1. Sampling and sample preparation

2.1.1. Sokli site

Samples of apatite ore (later referred to as 'S-O' with the sample numbers) and mill tailings (S-MT) were collected in 2010 from a former pilot scale phosphate mine at Sokli in Northern Finland. Pilot scale mining and mineral processing took place at the site at the end of the 1970s. Mineral processing did not include chemical treatment of the apatite

ore but was limited to mechanical removal of gangue minerals. The mill tailings were placed near the concentration facility in a tailing pond. Ore samples were collected from the former mining area from piles consisting of twelve different ores that had been mixed and crushed during processing. Samples of the mill tailings were collected from the tailing area. Three ore samples and three mill tailing samples were chosen for this study.

Ore samples were dried at 40 °C for 120 h and ground using a Mixer Mill Type MM-2 to fine powder. Mill tailing samples were already of sufficiently small grain size (<2 mm).

2.1.2. Talvivaara site

Samples of the black schist host rock (T-O) and mill tailings (T-T) were collected from the Talvivaara nickel mine located in Sotkamo, Eastern Finland in 2011. Talvivaara applies bioheap leaching to extract Ni, Zn, Cu and Co from the ore. Three different samples were chosen for this study: the primary ore before leaching (T-O-F), ore that had been leached for approximately 5 years (T-O-L) and a sample from the gypsum pond (T-T-1), where waste from the metal recovery process is discharged.

The same sample preparation procedure was followed as per samples from Sokli site.

2.2. Characterization techniques

2.2.1. X-ray fluorescence (XRF)

Portable XRF was employed on Sokli samples without pre-treatment to estimate the bulk composition and thorium content of the material on site. Analysis was carried out using a hand-held Thermo Scientific Niton XL3t 800 spectrometer in soil calibration mode. This instrument employs a miniature X-ray tube for excitation with a high performance, solid state Si-PIN detector. Each analysis was conducted over 90 s comprising three sequential 30 second cycles at each filter setting (15, 40 and 50 keV, respectively).

2.2.2. Gamma spectrometry

Gamma spectrometry was used for the determination of uranium and thorium from ground samples. Uranium was measured with the aid of gamma emission of the progeny nuclide ^{234m}Pa in equilibrium with ²³⁸U and ²³²Th with the aid of the progeny nuclides ²²⁸Ac and ²¹²Pb. The samples were counted on a Canberra BE5030 HPGe detector (diameter 82 mm, efficiency at 1.3 MeV ~ 50%). Prior to analysis, the detector was calibrated with a multi-nuclide standard (NPL) of identical geometry. The spectra were analyzed using Gamma99-spectral analysis software.

2.2.3. X-ray diffraction (XRD)

The samples were analyzed with XRD to identify, semi-quantitatively, the main minerals present. Analyses were performed using a Philips X'Pert MPD diffractometer. The X-ray diffraction spectra were recorded from 2 to 70° 2θ (step size 0.02° θ, time per step 1.00 s). The minerals were identified with PANalytical X'Pert HighScore Plus-program using the ICDD pdf-4/minerals database.

2.2.4. Electron probe micro-analysis (EPMA)

The samples were analyzed by electron probe micro-analyzer to identify the uranium and thorium-bearing minerals. Analyses were performed by wavelength-dispersive spectroscopy using a Cameca SX100 instrument. Analyzing conditions were as follows: accelerating voltage 15 kV, beam current and diameter 10 nA and 1–5 μm, respectively. Natural minerals and metals were employed as standards. Analytical results were corrected using the PAP on-line correction program (Pouchou and Pichoir, 1986).

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