

## Analyses of oxyanion materials by prompt gamma activation analysis

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Prompt gamma activation analysis (PGAA) has been used to analyze metal ion oxyanion materials that have multiple applications, including medicine, materials, catalysts, and electronics. The significance for the need for accurate, highly sensitive analyses for the materials is discussed in the context of quality control of end products containing the parent element in each material. Applications of the analytical data for input to models and theoretical calculations related to the electronic and other properties of the materials are discussed.

### Introduction

Elemental analyses for a wide array of elements in the Periodic Table are of extreme value for a wide range of purposes, including trying to gain a knowledge of materials failure when it occurs, modeling the electronic, magnetic, and chemical properties, and assessing and verifying quality control of the purity of the materials in which they are found. Both the elements and their compounds are useful for an extremely wide variety of applications in chemistry and materials science, including applications that are dependent on the elements' magnetic, electronic, and physical properties as well as their ability to form compounds and complexes. In obtaining precise analytical data for materials, the analyst may need a technique which will give really good, high-quality analytical data while preserving the integrity of the samples for archival purposes.

The materials that have been analyzed in the present study represent an eclectic group of elements that are important from a wide number of standpoints. Additionally, in many cases, the counteranions associated with the central elements in the materials can be of extreme importance in the compound's role as synthetic precursors for other materials where the original materials or compounds have really good advantages as starting materials. Beryllium nitrate, for example, can be used as a starting material for the synthesis of beryllium oxide,<sup>1</sup> which is used in an extremely wide variety of applications ranging from sophisticated electronic materials<sup>2</sup> to dopants in gemstones<sup>3</sup> to dental materials.<sup>4</sup> It also represents, however, an element whose toxicity in humans<sup>5,6</sup> makes it extremely important as an analytical target due to many applications that impact both humans and the environment. Magnesium sulfate is widely used in medical and biomedical applications,<sup>7</sup> while scandium

and its compounds (including the sulfate analyzed here) act as precursors in the synthesis of materials as well as serve as materials on their own.<sup>8</sup> Antimony is used in a wide variety of applications employing mixed elemental oxides, including catalysts, alloys, and magnetic materials.<sup>9</sup> Gallium is used for a wide assortment of electronic materials such as gallium arsenide,<sup>10</sup> many of which demand extremely high purity and quality control. Lead has applications in materials including powders, electronic devices, and ceramics<sup>11</sup> and also an extensive biochemistry and toxicology,<sup>12</sup> all areas of interest areas necessitating the ability to obtain definitive analyses. Thorium and uranium<sup>13</sup> are major members of the actinide, or *5f* block, of elements in the Periodic Table that are used as nuclear fuels, catalysts, and for many other applications.<sup>14</sup>

Neutron induced prompt gamma activation analysis (PGAA) is a non-destructive, self-calibrating, radioanalytical method capable of simultaneously identifying nearly the entire Periodic Table. It exploits the prompt capture gamma-rays themselves, while neutron activation analysis (NAA) utilizes the delayed gamma-rays from the radioactive daughter nucleus and is thus able to detect every element in the Periodic Table from hydrogen through uranium. The method has been applied to materials science, chemistry, geology, mining, archaeology, environment, food analysis, medicine and other areas. Development of high flux neutron generators and a new analytical PGAA database make it possible to apply PGAA/NAA techniques without requiring a nuclear reactor. The nuclear reactions to form the gamma-ray lines are independent of the physical form of the sample being analyzed, thus allowing the elemental composition of solids, liquids, and gases to be obtained. Also, the technique allows for the non-destructive analyses of samples with no prior chemical or other type of physical or experimental preparation.

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The present report describes the application of PGAA to the analysis of a wide array of chemically-based materials for which total characterization data, including those for trace contaminants, are often required. The technique also is discussed with respect to its use in monitoring trace amounts of elements used in the syntheses and processing of other materials that use such rare earths as precursor materials or as the desired final product.

## Experimental

### Materials

The elemental oxyanion samples were analyzed using prompt-gamma activation analysis as previously described.<sup>15-17</sup> The compounds of beryllium, magnesium, scandium, antimony, gallium, lead, thorium, and uranium were obtained commercially as being reagent grade (Table 1).

### PGAA method

The neutron-induced prompt gamma activation analyses (PGAA) were performed at the Institute for Isotopes and Surface Chemistry, Budapest, Hungary, which had been described previously.<sup>15-17</sup> The Budapest Reactor is a water-cooled, water-moderated research reactor with a thermal power of 10 MW. A beam of low-energy neutrons are transported for approximately 35 meters from the reactor core by a curved neutron guide fabricated from a glass coat with a nickel reflector. The prompt gamma experimental apparatus is located at the end of the guide where the energy of the neutrons is less than that of thermal neutrons due to the higher energy neutrons not being reflected. The thermal-equivalent effective flux is approximately  $2.5 \cdot 10^6 \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$  at the target position.

The samples were placed directly in the beam that had been collimated to an area of  $2 \times 2 \text{ cm}^2$ . The determined chemical composition of the sample was an average value for the entire irradiated volume of the sample due to the almost total transparency of the sample to neutrons. The prompt gamma-rays were detected by a detector system<sup>15</sup> whose main component was a Canberra high-purity germanium (HPGe) detector which was surrounded by a bismuth germanate (BGO) scintillator annulus used to reject Compton-scattered photons. The detector assembly could be moved to variable lengths from the target, with the main detector being moved to within as close as 12 cm to the target. Complete details of the experimental arrangement and detector system have been published elsewhere.<sup>16</sup>

Spectra for the samples were collected using a 16,000-channel multichannel analyzer from Canberra, Model No. S100 MCA. The energy and efficiency

calibrations for the system were made using known  $\gamma$ -lines emitted by radioactive sources and  $(n,\gamma)$  reactions. The collected spectra of the rare earth oxides were analyzed by "Hypermet PC," a  $\gamma$ -spectrum analysis program developed at our laboratory at the Institute for Isotopes and Surface Chemistry in Budapest.<sup>17</sup>

### Element identification

The elemental identification involved with these samples is based on the nuclear database at the Institute for Isotopes and Surface Chemistry, Budapest, Hungary. The elements are identified according to the energy values of their most intense prompt gamma-peaks (Fig. 1). The reliability of the element identification is controlled through different statistical parameters which are derived from the deviations of measured energy and intensity values from literature values.<sup>18</sup> The intensity ratios between the different gamma-peaks must also be considered, along with the possible background lines. The background gamma-rays mostly originate from the  $(n,\gamma)$  reactions in the surrounding material. The most important sources are from oxygen and nitrogen in the air, iron and aluminum in the equipment's material, and fluorine from the Teflon packaging material surrounding the samples.

### Determination of the chemical composition

The detected gamma-ray intensity, represented by the peak area ( $A_E$ ), is directly proportional to the mass of a given chemical element, and the measuring time,  $t$ . Hence:

$$m = \frac{1}{S} \cdot \frac{A_E}{t} \quad (1)$$

$$\text{where } S = \frac{N_A}{M} \cdot \theta \cdot \sigma_0 \cdot I_\gamma \cdot \Phi_0 \cdot \varepsilon(E_\gamma) \quad (2)$$

is the analytical sensitivity, expressed in units of  $\text{counts} \cdot \text{s}^{-1} \cdot \text{mg}^{-1}$ . It is proportional to the neutron capture cross section of the nucleus  $\sigma_0$ , the isotopic abundance  $\theta$  and the gamma-yield  $I_\gamma$  which are nuclear constants, as well as to the neutron flux  $\Phi_0$  and the detector efficiency  $\varepsilon(E_\gamma)$  – which are characteristics of the measuring system.

The mass ratio for an element  $x$  can be determined according to the following equation:

$$\frac{m_x}{m_R} = \frac{A_{E,x}}{A_{E,R}} \cdot \frac{k_{0,C}(R)}{k_{0,C}(x)} \cdot \frac{\varepsilon_R(E_\gamma)}{\varepsilon_x(E_\gamma)} \quad (3)$$

where  $R$  is an arbitrary reference element contained in the sample. This ratio is independent of the neutron flux, it depends only on nuclear constants and the detector efficiency. The latter are known with good accuracy.<sup>19</sup>

The  $k_0$ -factors were determined by internal standardization measurements. The masses were calculated according to Eqs (1)–(3). The gamma-lines used and the corresponding  $k_0$ -factors are listed in Reference 19. The possible interferences between different gamma-peaks were individually examined, and the peaks affected by spectral interference were neglected.

The total uncertainties (standard deviations) were calculated from the statistical (counting) uncertainties of the peak areas, the uncertainties of the  $k_0$ -factors and the uncertainties of the detector efficiencies. As the last two typically have standard deviations of a few per cent, the total uncertainty is mainly determined by the counting statistics reflected in the analytical sensitivities.

#### Detection limits

For the un-detected elements, detection limits ( $C_L$ ) were calculated from the spectra themselves from Eq. (4), where  $\sigma_B$  is the standard deviation of the baseline, and  $S$  is the sensitivity for a given element. The baseline is a complex function that was calculated by the Hypermet PC:

$$C_L = 3\sigma_B/S \quad (4)$$

automatically for each region,  $\sigma_B$  is the constant part of the function.

#### Measurements

Elemental compositions of the samples were obtained by means of PGAA. The oxyanion compounds were run as solid powders as received. Compton suppressed prompt gamma-ray spectra were measured as usual. The samples were irradiated for ~900 to 61,000 seconds.

## Results and discussion

From a material standpoint, the production quality and purity of a material are extremely important with

respect to a whole analysis of the material. Because of different feedstocks of raw materials – such as ores – are used for the production of many batches worldwide of chemicals and materials from the parent elements are used to make other materials, there is usually a wide assortment of impurities and levels of impurities observed in the final product. This is possibly due to the processing and separation scheme used to extract the parent elements of each material from their ores and subsequent processing and purification. A thorough analytical knowledge of solid matrix elements can be very important from several standpoints, with either the element of interest being the primary element of the bulk material matrix itself, or a contaminant in the material matrix. Indeed, entire books address the subject of such chemical defects and impurities in a wide variety of materials.<sup>20,21</sup> Many times, it is important to have a precise and very accurate analysis of a material with respect to the concept of quality control. This is true in the material manufacturing sector, where the bulk material must have extremely low levels of impurities because of the impurities' possible effect on the performance characteristics of a particular material. It is also beneficial to know the levels of contaminant elements in industrial batches of materials in general, to be able to use this knowledge to understand the causes and postulate mechanisms in case of material failures.

The need for a detailed knowledge of contaminants in solid matrices also is extremely helpful in the development of models and theoretical calculations of processes involving electronic materials. In the case of semiconductors, for example, contaminants of different elements are critical to both the quality and performance of the material. This leads to a variety of questions with respect to the nature and number of these elemental contaminants in the lattice. What is the concentration, coordination sphere (types and number of next nearest atoms), oxidation state, and electronic/magnetic state of each contaminant? Also, are there electronic and magnetic interactions among contaminant elements in the lattice? All of these questions are applicable to manganese and iron shown in Table 2, for example.

Table 1. Analysis conditions of metal oxyanion materials by PGAA

Element (anion)	Sample	Measurement time, s	Total counts
Beryllium (nitrate)	Be(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	64,050	487,313
Magnesium (sulfate)	MgSO <sub>4</sub> ·7H <sub>2</sub> O	15,806	548,355
Scandium (sulfate)	Sc <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	12,000	3,981,050
Antimony (sulfate)	Sb <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	8404	2,386,684
Gallium (nitrate)	Ga(NO <sub>3</sub> ) <sub>3</sub> ·8H <sub>2</sub> O	5674	140,782
Lead (nitrate)	Pb(NO <sub>3</sub> ) <sub>2</sub>	43,920	337,998
Thorium (nitrate)	Th(NO <sub>3</sub> ) <sub>4</sub> ·4.5H <sub>2</sub> O	61,903	2,586,834
Uranium (acetate)	UO <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	67,811	29,641,663

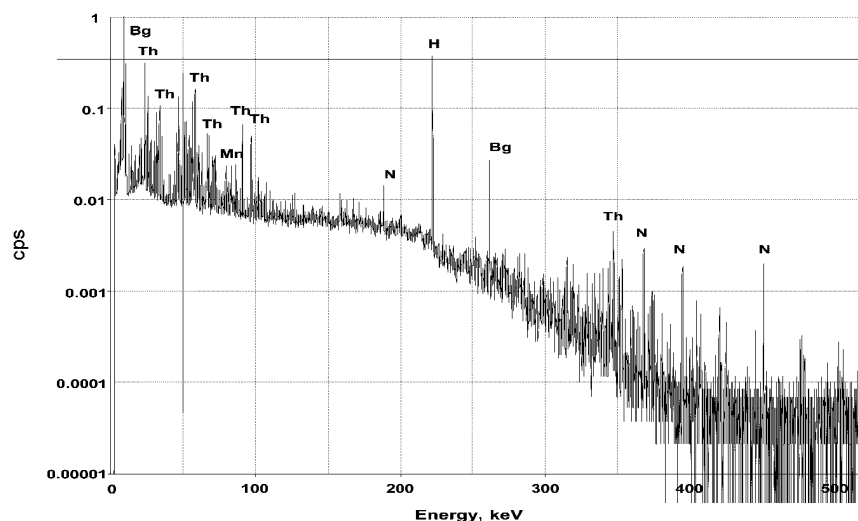
Fig. 1. PGAA spectrum of  $\text{Th}(\text{NO}_3)_5 \cdot 4.5\text{H}_2\text{O}$ 

Table 2. Contaminant elements and concentrations found in oxyanion materials

Element (anion)	Sample	Contaminants
Beryllium (nitrate)	$\text{Be}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	B, 0.39 ppm; Cl, 14(3) ppm; Cd, 0.14 ppm
Magnesium (sulfate)	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	Cl, 17(2) ppm; Fe, 0.070(14) %; Sm, 0.6(2) ppm
Scandium (sulfate)	$\text{Sc}_2(\text{SO}_4)_3$	No minor elements detected
Antimony (sulfate)	$\text{Sb}_2(\text{SO}_4)_3$	No minor elements detected
Gallium (nitrate)	$\text{Ga}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$	No minor elements detected
Lead (nitrate)	$\text{Pb}(\text{NO}_3)_2$	Fe, 430(100) ppm
Thorium (nitrate)	$\text{Th}(\text{NO}_3)_4 \cdot 4.5\text{H}_2\text{O}$	Mn, 0.020(5)%
Uranium (acetate)	$\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$	No minor elements detected

## Conclusions

Prompt gamma activation analysis (PGAA) has been used to analyze metal oxyanion materials for the determination of small dopant amounts of elemental impurities. The technique proves to be effective as an analytical approach in which the original sample is preserved with no damage or loss of mass from sampling, giving to the investigator an analytical method that is free from additional chemistry, separation procedures, or scientific labor to prepare the sample for analysis. Because of this, the sample is available for archival storage after the analysis.

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