Comparative use of INAA and ICP-MS methods for environmental studies

G. Revel,* S. Ayrault

Pierre Sue Laboratory (CEA-CNRS) C.E. Saclay – B 657 – F91191 – Gif sur Yvette Cedex, France

(Received November 22, 1999)

The advantages and drawbacks of using instrumental neutron activation analysis (INAA) and inductively coupled plasma mass spectrometry (ICP-MS) for soil, sediment, plant and water pollution studies are discussed. The experimental procedures used for each method and for each type of sample matrix are described. They were tested on several certified reference materials. The results obtained on these materials showed good agreement for many elements for which the two techniques are suited, and they were complementary for the other elements which are also of environmental interest. An element-by-element assessment is presented to indicate the precautions to be taken and the most convenient technique for each of them.

Introduction

Environment studies have become increasingly important, in both industrialized and developing countries. These studies need to be able to analyze many elements over a very wide range of concentrations. Many methods can be used, but two appear to be particularly interesting for mineral pollutants: neutron activation analysis (NAA) and inductively coupled plasma mass spectrometry (ICP-MS). These methods can determine multiple elements and isotopes and are very sensitive, but differ greatly in their operating principle and use. NAA is an old method, first described in 1936 by HEVESY and LEVY.¹ This method has long been the only one sensitive and accurate enough for trace and ultra-trace analyses. More modern easier to use methods have never completely replaced NAA. ICP-MS, which combines excitation at the very high temperature obtained in a plasma of argon with detection by mass spectrometry, has recently been adopted by a large number of laboratories. This method seems to have several advantages over NAA (great sensitivity for determining a wide range of elements, easy access and high sample throughput). Both these techniques are used in our laboratory. We have therefore applied them to study soil, water and air pollution. The analytical procedures are well developed and were regularly tested on certified reference materials. We have compared results to identify the best method for analyzing a particular matrix and set of elements. Both methods have been used to analyze samples of soils, sediments, plants and water. For example, they were used to analyze the impact of rare earth elements on rice crops.² The use of small quantities of rare earth compounds as fertilizers (100–300 g/ha) increases the yield (plus 10–15%), quality of seeds and the resistance of rice to saline conditions.³ River pollution has been studied by analyzing sediments and water. The origin and extent of pollution were specified and quantified. Studies in Meknes city (Morocco), where the water is polluted by waste originated by rejection from local craftsmen,⁴ in Brazil, on mining effluents in the State of Minas Gerais,⁵ and agricultural pollution caused by cacao growing in the State of Bahia,⁶ were carried out. Analysis of mosses provided a precise chart of the heavy metal deposits in France,⁷ complementing the data available for the whole of Europe.⁸ Lichens are also used as bio-indicators in volcanic areas.⁹

Experimental

Sampling, storage and sample preparation

The environmental study was divided into five steps: analytical planning, representative sampling, sample preparation, analysis and data evaluation. Each step involved errors. The difficulty and susceptibility to error of each investigation depended on the sample matrix and content of elements to be analyzed. The difficulty of sample preparation depended on the form required by the analytical method used (solid for INAA and solution for ICP-MS).

Heterogeneous solid samples, like soils, plants or sediments, can be stored without any particular difficulty. The analytical step most susceptible to error was sampling. Some practical basic rules can be helpful: avoid contamination by the container, take a primary sample as large as possible, use a random division of the area to be sampled. International norms are available (e.g., AFNOR standard ref. 31–100 and 101 for sampling soils).¹⁰ The quality assurance of plant sampling and storage has been fully described by MARKERT.¹¹ Sample washing, drying, homogenization, aliquoting, and decomposition, were also potential sources of error. Certified reference materials (CRM) were used to check for sample loss or contamination.

* E-mail : grevel@drecam.cea.fr

© 2000 Akadémiai Kiadó, Budapest

Kluwer Academic Publishers, Dordrecht
Taking water samples was easy, but their preservation during their transport from the field to the laboratory and their storage was much more delicate. Acidification to pH 2 with ultra-pure HNO₃, the use of polypropylene bottles (Nalgene®) and storage at low temperature (4 °C) as soon as possible after sampling all helped to preserve samples for several months. Nevertheless, samples were filtered prior to acidification to prevent the dissolution during acidification of trace elements adsorbed onto suspended matter and colloids. And filtration in the field was very susceptible to contamination. Vacuum filtration systems were found to be more appropriate for turbid waters than those using positive pressure. Cellulose ester and polycarbonate caused the least contamination, but polycarbonate filters were difficult to handle.

**Neutron activation analysis (NAA)**

Solid samples were dried, crushed in an agate mortar and homogenized. Aliquots of powder (50–150 mg) were compressed to give pellets 10 mm in diameter. They were wrapped in high purity aluminum foil and placed in the shuttle used for irradiation, with the flux monitors and CRM prepared in the same manner.

Because of the radiolysis effect, aqueous samples were converted to solids before irradiation for NAA. Samples (10 ml) were evaporated in ultrapure quartz vials at 80 °C for 24 hours. The vials had been cleaned with hydrofluoric acid, rinsed with ultra-pure water and dried. Three vials containing samples and an empty vial were then sealed by fusion and were irradiated at the same time as the flux monitor. Aqueous CRM samples were prepared in the same manner.

All irradiations were performed in the ORPHEE and OSIRIS reactors at the Nuclear Center, Saclay. The Pierre Site Laboratory is directly connected by pneumatic or hydraulic conveyors to six irradiation positions in these reactors. The characteristics of the neutron fluxes available are shown in Table 1.

As environment research requires analysis of many samples, we used instrumental analysis (INAA). The irradiation and measuring conditions were chosen as a function of the samples analyzed and the elements determined. Brief irradiations (30 seconds to 1 minute) (Al, Dy, Mg, Ti, V determinations) or 30 minutes (Cl, Mn, Na, W determinations) in positions P1 and P2 in the ORPHEE reactor were used for solid samples. Longer irradiations (3 to 72 hours) in positions P3 or P4 were used for Ce, Co, Cr, Fe, etc. Positions H1 and H2 in the OSIRIS reactor were used for epithermal reactions ⁴⁷Ti(n,p)⁴⁷Sc, ⁵⁸Ni(n,p)⁵⁸Co, ⁵⁴Fe(n,p)⁵⁴Mn, etc. Irradiations were then often performed under a cadmium coating to select epithermal and rapid neutrons.

The sodium in the quartz tubes allowed analysis of only the elements giving long half-life radionuclides in aqueous samples after a 16 hour irradiation and a decay time of 10 and 20 days before measurements.

The gamma-radioactivity was measured with a 100 cm⁻³ coaxial ultra-pure germanium crystal coupled to a 4096 pulse-height analyzer. Several measurements were made on each sample after increasing cooling times. The concentrations were calculated using the in-house program K₉LABSUE, written in Turbo Pascal. This is a quasi independent data format package for kᵣ quantification based on the method developed by DE CORTE. Gold monitors were used for short irradiations and iron and zirconium monitors for long irradiations.

**Inductively coupled plasma mass spectrometry (ICP-MS)**

Environmental studies require determination of the total content of the sample, not just the more soluble part. Solid samples must be dissolved prior to ICP-MS analysis, which may be the most difficult part of the analysis. Losses and contamination have to be avoided. Many methods for the total dissolution of sediments, soils and plants have been published. We tested different wet and dry methods, in closed and open systems.

Plants (rice, mosses, lichens) were digested in microwave in open PTFE vessels (Microdigest A301, Prolabo, France). Nitric acid, hydrogen peroxide and hydrofluoric acid were added successively (5 ml each). The samples were reduced to dryness, then taken up in 3 ml nitric acid. They were again evaporated to dryness and taken up in 10 ml water. The digestion solution was poured into polyethylene flasks that had been washed with 2% nitric acid. The PTFE vessels were cleaned (boiling 1+1 HNO₃+H₂O) between samples.

<table>
<thead>
<tr>
<th>Nuclear reactor Channel</th>
<th>OSIRIS (70 MW)</th>
<th>ORPHEE (14 MW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₁, H₂, P₁ and P₂, P₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal neutrons (E = 0.025 eV)</td>
<td>0.77 × 10¹⁴</td>
<td>1.2 × 10¹⁴</td>
</tr>
<tr>
<td>Epithermal neutrons (E&gt;0.1 eV)</td>
<td>1.9 × 10¹²</td>
<td>4.1 × 10¹²</td>
</tr>
<tr>
<td>Fast neutrons (E&gt;0.5 MeV)</td>
<td>9.6 × 10¹²</td>
<td>2.3 × 10¹³</td>
</tr>
</tbody>
</table>

Table 1. Neutron irradiation facilities at the Pierre Site Laboratory (n cm⁻² s⁻¹)