210Pb and 210Po analysis in sediments and soils by microwave acid digestion

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A microwave acid digestion method prior to the determination of 210Pb and 210Po in sediments and soils is described. It involves an acid (HNO3, HCl, HF and H3BO3 mixture) digestion with microwave heating in closed vessels at high pressures. Analyses carried out for various reference materials showed that the results were statistically equal to certified values and reproducibility was also assured. The advantage of the microwave technique compared to the traditional leaching procedures is that the solid materials are completely dissolved and, therefore, ca. 100% efficiency is achieved in the extraction of 210Pb and 210Po, even though a fraction is associated to the silica net. Moreover, time of analysis is drastically reduced, as are the risks associated to vapour inhalation and material corrosion.

Introduction

The knowledge of the rate at which particulate suspended matter is accumulating now, and has accumulated over the past few hundred years in the bottom sediment of aquatic systems, is essential to understand the biogeochemical processes that take place in those environments.1,2 During the last decades, 210Po and 210Po, both members of the 238U radioactive decay chain, have become two of the most useful and widely used radioactive tracers to study such processes. The relative insolubility of 210Pb in the water column and its half-life (22.3 y) makes it suitable to study the mixing and sedimentation rates for recent lacustrine, estuarine or marine sediments.3,4 On the other hand, the 210Po/210Pb ratio is a key parameter to identify the biogenic or lithogenic origin of particulate matter in coastal areas.5-7

The increasing interest in this kind of studies makes it necessary to establish a precise analytical method which is easy to apply to a large number of samples in a short period of time. The methodology usually used to determine 210Pb and 210Po activities in sediment trap material or bottom sediments includes three phases: (1) acid digestion of the sample, (2) spontaneous deposition of polonium isotopes on a silver disk and (3) measurement of 210Po radioactivity by α-spectrometric techniques.210Pb activity is assumed to be identical to that obtained from 210Po, as both radionuclides reach radioactive equilibrium after six months in closed systems. For recent sediments (<1 year), such as those obtained from sediment traps, a second deposition of polonium isotopes, after 210Po ingrowth from 210Pb, is needed to determine the 210Pb contents.6 Direct counting of samples by γ-spectrometry can also be used, though long counting times and difficulties in calibration make the technique difficult to use in experiments with very small samples of a varied nature.

Sample pre-treatment is one of the most time-consuming steps. After drying, the sample is usually wet ashed in open beakers using mixtures of various acids such as HCl, HNO3, HClO4 and HF2 in different proportions, heating temperatures and contact times. The solution must be filtered before the elimination of nitric acid, making the resulting solution 0.3-1 mol/1 HCl.8-10 Such a leaching procedure does not completely dissolve the silica present in the sample and the trace elements absorbed in it. Furthermore, the analyst can not know the degree of dissolution of the material reached in each analysis. It is worth emphasising that even the use of an internal radioactive tracer does not compensate for incomplete digestion.

The methods used to interpret the 210Pb activities observed or, in case of sediment profiles, the dates and accumulation rates, rely on the estimation of the unsupported 210Pb, defined as the difference between the total 210Pb and the in situ or supported 210Pb formed from terrigenous 226Ra present in the sample.6,11,12 Therefore, to interpret accurately, digestion should be complete, and use of HF in the digestion process to remove the insoluble materials, such as silica, appears to be essential.13

Both leaching and conventional total digestion methods in open systems (e.g., on a hot plate) have some other disadvantages, as they are slow and require close attention to the risks of external sample contamination, formation of insoluble salts during evaporation, exposure to acid fumes and corrosion.13 Reaction temperature is also limited to the atmospheric boiling point of the mixture. In order to avoid these problems, wet digestion can be carried out making use of microwave heating in closed vessels.

In this paper we describe a microwave dissolution method prior to the measurement of 210Po and 210Pb in solid samples in order to assure a complete digestion of...
the material, reduce analysis time, minimise contamination and health risks, and obtain maximum reproducibility. Diverse sediment and soil reference samples were analysed using this methodology and results were compared with those obtained from leaching experiments and the certified activities.

**Experimental**

**Samples**

The reference samples analysed were: (1) IAEA–326: black soil from the Kursk region, dried, milled using a vibration mill and homogenised; (2) IAEA–327: podsollic soil from the Moscow region, dried, milled using a vibration mill and homogenised; (3) IAEA–300: bottom sediment collected from the Bothnian Sea (Baltic Sea), dried, ground in a ball mill and homogenised; (4) MAST–SED: bottom sediment collected from El Fangar (Ebroad Delta, Spain), dried, homogenised to a fine powder with a ball mill; and (5) MAST–TRAP: collected from Gulf of Biscay (north-eastern Atlantic, ECOMARGE experiment) with a PPS–5 sediment trap. Homogeneity of the distributed aliquots during the intercomparison exercises was assured by the organising laboratories by measuring the activity of several $\gamma$-emitters in random samples. This was not necessary for MAST–TRAP, as homogeneity is assured due to the processing method after collection.

Samples IAEA–300, IAEA–326 and IAEA–327 were certified through intercomparison exercises organised by the International Atomic Energy Agency (IAEA), and recommended $^{210}$Pb specific activities are available. MAST–SED and MAST–TRAP were used for laboratory intercomparison exercises in the frame of the EUROMARGE–NB (MAST) project. A marine sediment sample, FLG107, collected from the Fonera canyon (north-western Mediterranean), was dried, homogenised, and used to verify the reproducibility of $^{210}$Pb analysis by microwave digestion.

**Equipment**

Leaching digestion was performed in open beakers by heating on a commercial SBS–2000 hot plate (SBS Instruments, Badalona, Spain) equipped with nine magnetic stirrers with independent speed regulators. Total sample digestion was accomplished with the use of a commercial MDS–2000 Microwave Sample Preparation System (CEM, Matthews, NC, USA). The system is provided with a 630 W – 2450 MHz magnetron, programmable in 1% power increments, to control the heating rate. An internal pressure gauge allows pressure to be controlled from 0 to 1.38 MPa (200 psi). Up to thirty energy and time multi-step procedures, consisting of up to five stages each, can be programmed with a digital computer. The microwave oven cavity is coated with a corrosion resistant fluoropolymer and equipped with a variable speed exhaust blower to remove vapours. Three door interlocks and an interlock monitoring system prevent microwave emission when the door is open. Samples placed inside vessels are exposed to rapid heating and elevated pressures, causing the samples to dissolve in a short time.

**Reagents**

Acids used during both microwave and leaching experiments were Merck pro analysis for HCl (32% m/v), HF (40% m/v) and H$_3$BO$_3$ (2.5% m/v), and Merck extra pure for HNO$_3$ (65% m/v). Water purified with a Milli-Q system (Millipore) was used throughout the analyses. Radiochemical tracer $^{209}$Po (0.1229 ± 0.0017 Bq ml$^{-1}$) was provided by IAEA. Silver discs

<table>
<thead>
<tr>
<th>Material</th>
<th>Reference value</th>
<th>This work</th>
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<tbody>
<tr>
<td></td>
<td>Mean, Bq kg$^{-1}$</td>
<td>Confidence interval, Bq kg$^{-1}$</td>
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<td>IAEA–326</td>
<td>Soil</td>
<td>45.7</td>
</tr>
<tr>
<td>IAEA–327</td>
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<td>MAST–TRAP</td>
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</table>

Confidence intervals and quoted uncertainties correspond to ± 2σ.