

The Production and use of $^{197}\text{Hg}^g$ Radiotracer to Study Mercury Transformation Processes in Environmental Matrices

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Abstract: This work shows the applicability of the radiotracer $^{197}\text{Hg}^g$, which was employed successfully in mercury methylation/de-methylation experiments in soils and sediments. This radiotracer can be produced in non-high flux reactors, using non-enriched Hg. The experiments consisted of amending triplicates sediment and soil samples, and incubating with labeled Hg for different time periods. HgCH_3^+ was extracted using toluene. The specific activity of $^{197}\text{Hg}^g$ obtained was high enough to allow minimum addition of total mercury to our experiment design of 5-10 ng, which is comparable to the radiotracer ^{203}Hg and other non-radioactive tracers used for this purpose. HgCl_2 was irradiated to produce $^{197}\text{Hg}^{2+}$ tracer, while HgCH_3Cl was used for $^{197}\text{HgCH}_3^+$. Well, coaxial, and planar HPGe detectors were used in the experiments to measure the radiotracer. Spectra peaks associated to $^{197}\text{Hg}^g$ decay were determined by using usual peak fitting programs and also by direct spectrum integration.

Key words: radiotracer, ^{197}Hg , Hg methylation, Hg de-methylation.

INTRODUCTION

The use of radioisotopes to trace different transport and transformation processes is widespread; in the case of mercury the most frequently used radiotracer is ^{203}Hg , which in recent years is no longer regularly produced and therefore difficult to purchase. However, when adequate facilities are available $^{197}\text{Hg}^g$ can be also employed successfully, as it was demonstrated in mercury methylation/de-methylation in soils and sediments performed at the Department of Environmental Sciences, Jozef Stefan Institute, and Laboratorio de Análisis por Activación

Neutrónica, Centro Atómico Bariloche. $^{197}\text{Hg}^g$ ($T_{1/2}=64.14$ h; TULI, 2000) can be produced in a research nuclear reactor by irradiating non-enriched Hg targets with thermal neutrons (for the $^{196}\text{Hg}(n,\gamma)^{197}\text{Hg}^g$ reaction $\sigma_{\text{th}}=3080\pm 180$ b; production with epithermal neutrons is not relevant: $I_g=413\pm 15$ b; MUGHABGHAB, 1981). $^{197}\text{Hg}^m$ ($T_{1/2}=23.8$ h; TULI, 2000) is also produced, and 93 % of its decay feeds the ground state, but with 30 times less probability ($\sigma_{\text{th}}=109\pm 6$ b and $I_\gamma=58.9\pm 2.4$ b; MUGHABGHAB, 1981). Figure 1 shows the decay scheme of ^{197}Hg . $^{197}\text{Hg}^g$ has a production rate, for short irradiation periods, about 50 times higher than

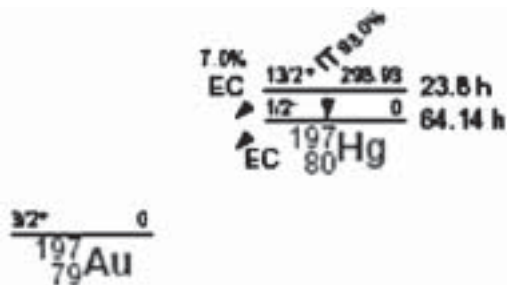


Figure 1. Decay scheme of ^{197}Hg (FIRESTONE, 1996).

that of ^{203}Hg , and hence it is possible to produce it with high specific activity in shorter irradiations, in non-high flux reactors (10^{12} to 10^{13} $\text{n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$), using non-enriched Hg. Another advantage of the use of $^{197}\text{Hg}^g$ to trace processes is that, because of its short half life, the cleaning of devices and tools of the $^{197}\text{Hg}^g$ contamination associated to their use or caused by accidents, can be done just letting the tracer to decay away, hence assuring no interference from previous experiments.

RESULTS AND DISCUSSION

For the methylation/de-methylation experiments in soils and sediments, HgCl_2 was irradiated to produce the $^{197}\text{Hg}^{2+}$ tracer, while HgCH_3Cl was used to produce $\text{CH}_3^{197}\text{Hg}^g$. In both cases the tracer is ready to be used after a few hours of cooling time, to allow ^{38}Cl ($T_{1/2}=37.24$ m; TULLI, 2000) to decay. HgCl_2 was dissolved in 3.2 % HNO_3 after irradiation, and HgCH_3Cl was dissolved in isopropanol. Working solutions of both mercury compounds were prepared by appropriate dilution. Since the HgCH_3Cl decomposes during irradiation, purification has to be done immediately before each application. HgCH_3^+ and Hg^{2+} in 6M HCl solutions were separated by anion exchange chromatography (Dowex 1x8

resin, Cl-form, 100-200 mesh) using minimal light conditions. The HgCH_3^+ is then collected and the solution neutralized for further tracer experiments. In our experiments we observed about 20 % decomposition of HgCH_3Cl during irradiation (20 h in 10^{12} $\text{n}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ thermal neutron flux).

The more relevant emissions associated to $^{197}\text{Hg}^g$ decay are X-rays 67.0 keV (21 %), 68.8 keV (35 %) 77.9 keV (12 %) and 80.4 keV (3.3 %), and g-ray 77.3 keV (18 %) (BROWNE, 1986). Typical spectra obtained with high purity germanium detectors (HPGe) are shown in Figures 2 and 3. Spectra obtained with planar detectors (see Fig. 2) have higher resolution compared to the well detector, but the efficiency of the detection system is much lower. The peaks associated with 67.0 and 68.8 keV emissions are clearly defined in the spectrum collected with the planar detector (see Fig. 2), but they are not resolved when the well detector is used (see Fig. 3). The 77.3 and 77.9 emissions are included in a single peak, superposed to the 80.4 keV peak, in the spectrum collected with the well detector (see Fig. 3), but these two emissions can be distinguished, but not resolved, using the planar detector (see Fig. 2). HPGe detectors allow, in general, discriminating three main peaks by using usual peak fitting programs, namely 67.0 keV, 68.8 keV, and 77.3 + 77.9 keV. But the manual determination of peak areas in two regions, one including 67.0 and 68.8 keV X-rays, and the other including 77.3, 77.9, and 80.4 keV emissions, when low resolution detectors are used, also provide accurate results. This is because these kinds of studies imply relative measurements with respect to a reference, and no absolute measurements are required. Also direct spectrum

integration procedures are much simpler. This procedure can also be applied to the peak area determinations for the 77.3 + 77.9 keV region when high-resolution detectors are used. Well, coaxial, and planar HPGe detectors were used successfully in the experiments mentioned before. For very low activity measurements, X-rays generated in

the lead shielding (72.8 keV, 75.0 keV, 84.5 keV, and 84.9 keV) may affect the 77.3 + 77.9 keV measurement region of the spectra, but the 67.0 + 68.8 keV region remains undisturbed. The use of a 1 cm thick copper plate lining inside the shielding was effective to prevent the appearance of the Pb X-ray peaks in the spectrum.

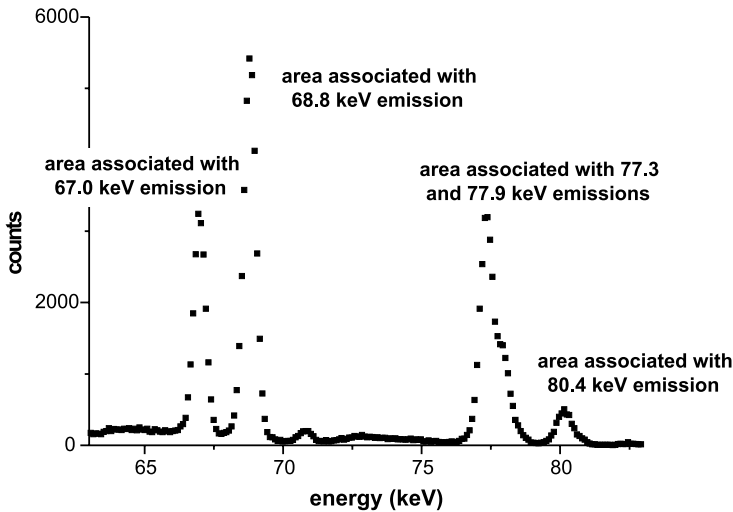


Figure 2. Spectrum obtained from a $^{197}\text{Hg}^{\text{g}}$ liquid source with an HPGe planar detector.

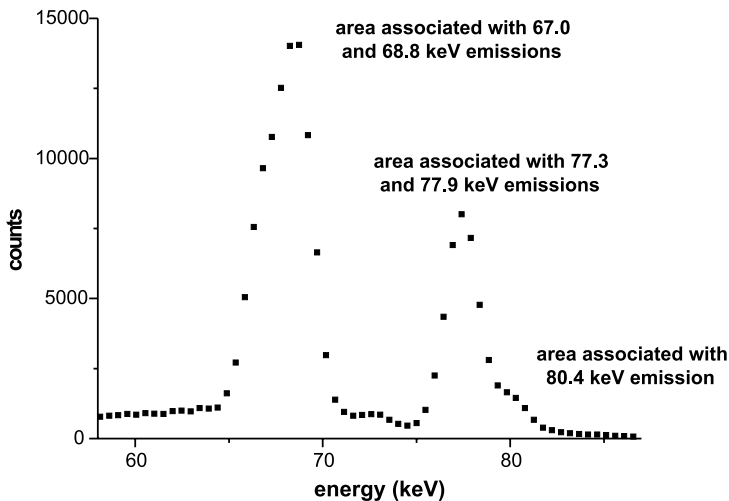


Figure 3. Spectrum obtained from a $^{197}\text{Hg}^{\text{g}}$ liquid source with an HPGe well detector.

By simple methylation/de-methylation experiments performed so far in soils and sediments the specific activity of $^{197}\text{Hg}^g$ was high enough to allow minimum addition of total mercury. Experiments consisted of amending triplicates sediment and soil samples, and incubating with labeled Hg for different time periods. In addition, blanks and samples in which microbial activity was inhibited by flash freezing just after inoculation (“killed control samples”) were also assayed. HgCH_3^+ was extracted using toluene, which was then dried using anhydrous Na_2SO_4 (MARVIN-DIPASQUALE, 2003). An additional clean-up step by aqueous solution of thiosulphate was used in lake sediment experiments, in order to examine the presence of inorganic Hg^{2+} in toluene extracts. Methylation experiments performed on sediments by incubation of labeled Hg^{2+} showed $^{197}\text{Hg}^g\text{CH}_3^+$ recoveries as low as $0.105 \pm 0.020\%$ to $0.133 \pm 0.018\%$ for toluene extraction on “killed control samples”, and $0.0354 \pm 0.0078\%$ to $0.0716 \pm 0.0035\%$, also on “killed control samples” using the more extensive extraction. Uncertainties reported are the standard deviations of triplicates. Total Hg inoculated in methylation experiments with sediments ranged from 50 to 100 ng.g^{-1} wet sediment, and Hg inoculated in de-methylation experiments with

soils ranged from 50 to 400 ng.g^{-1} . The specific activity of the radiotracer can be further improved with proper optimization of the irradiation; for our experiments design an inoculation of $5\text{-}10 \text{ ng.g}^{-1}$ can be achieved. The total Hg amounts of labeled Hg inoculated for the experiments performed are comparable to the amounts amended when ^{203}Hg and other non-radioactive tracers are used for this purpose. In addition, the sensitivity of the results strongly depends on experimental design and counting equipment.

The tracer allows an assessment of mercury methylation and de-methylation potentials in soil and sediments, and also mercury reduction potential. The latter is also very important to assess the mass balance of the added radiotracer. Appropriate separation procedures have to be employed, including solvent extraction for HgCH_3^+ and trapping of volatile mercury species, if present. In the case of reduction potential measurements, mercury can be trapped on solid adsorbents, such as gold traps for total gaseous mercury or Tenax if speciation of gaseous Hg is intended. Direct trapping of total gaseous Hg in aqueous solutions of permanganate is also possible. Based on trapping system an appropriate detection system should then be selected.

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