Measurement of carrier free $^{129}I/^{127}I$ in environmental samples by Accelerator Mass Spectrometry

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^{129}I is a radioisotope of iodine with a half-life of 15.7 My. In the pre-nuclear era, ^{129}I resulted primarily from spontaneous fission of ^{238}U, and cosmic ray induced reactions with the xenon component of the atmosphere. In the post-nuclear era, anthropogenic ^{129}I has resulted primarily from nuclear weapons testing, reprocessing of nuclear fuels, and accidental (example Chernobyl) or deliberate (activities of the former USSR in the Kara Sea) discharges of nuclear products into the environment. Potential uses of ^{129}I include monitoring of the environment around nuclear sites, as an oceanographic tracer, and as a retrospective proxy for ^{131}I dispersion (Yiou *et al.*, 1994). For many of these applications, the most relevant parameter is the ratio of ^{129}I to stable iodine (^{127}I) since this compensates for concentration and dilution processes in the hydrosphere and biosphere. In addition, use of the ratio $^{129}I/^{127}I$ automatically takes into account the efficiency of extracting iodine from the samples.

Because of its long half life, analysis of ^{129}I by radioactive decay is inefficient. While other techniques such as neutron activation, classical mass spectrometry, and laser spectroscopy have been used, the most dramatic improvement has been the application of accelerator mass spectrometry (AMS) (Elmore *et al.*, 1980, Kilius *et al.*, 1990). Like classical mass spectrometry, AMS measures relative isotopic ratios, which are translated into absolute ratios by comparison with a standard. The compound that has been found to be most convenient for AMS analysis is AgI. In most environmental samples, the quantity of ^{127}I in the sample is insufficient to give a quantity of AgI that is practical to manipulate. Therefore in general a few mg of carrier iodine is added at the beginning of the extraction process. However, if one wishes to have the $^{129}I/^{127}I$ ratio in the initial sample, it is necessary to make a separate determination of ^{127}I in an aliquot of the sample before addition of the carrier. Also, one must take precautions to ensure isotopic homogenization of the carrier with ^{129}I in the sample. Because of the potential volatility and multiple valence states of iodine, this is not always trivial especially for solid samples. It would thus be desirable to be able to make a carrier free determination of $^{129}I/^{127}I$ from environmental samples by AMS.

The procedure described here was developed initially to measure $^{129}I/^{127}I$ in sea water samples . In our normal procedure (Zhou, 1995) we generally use a 1 liter sample of ocean water, which typically contains ~50 ug of ^{127}I and 10–100 fg of ^{129}I. After taking a 10 ml aliquot for ^{127}I determination by colorimetry, we add ~3 mg of carrier iodine. Because of its affinity for iodine, it occured to us that it might be possible to react I_2 directly from sea water with metallic silver. To test this, we added 5–10 mg of Ag powder (Goodfellow AG006020/21) to 250–1000 ml of acidified ocean water (to liberate I_2). After agitation for several minutes, the solution was centrifuged and the Ag powder separated from the water. After washing the powder several times with distilled water, it was dried in an oven at 60°C. The powder was then pressed into a 1 mm diameter, 1 mm deep hole in a support used as a cathode in our caesium sputter ion source (General Ionex model 846). Cathodes prepared in this way were found to give 30–600 nA of I^- for at least 30 minutes, ample time to complete AMS measurement. AMS measurements were carried out at the recently installed heavy ion line at the Tandetron based AMS facility at Gif sur Yvette. At the high energy end of the accelerator, the currents of I^{5+} were 5 to 100 nA . Therefore, for samples having $^{129}I/^{127}I$ ratios of 10^{-10} the ^{129}I count rate was generally a few counts per second.

In addition to the much greater simplicity in preparing samples, this technique has several other advantages. (i) It avoids the necessity of a separate ^{127}I measurement. (ii) because of the simplified chemical treatment the potential for contamination is greatly reduced. (iii) it increases the measured ratio by almost 2 orders of magnitude, thus reducing the measuring time. (iv) the reduced beam intensity in our AMS system improves measurement precision.

We have observed with our normal samples that when we injected currents of > 3 uA , we often had current dependent $^{129}I/^{127}I$ ratios, presumably due to space charge effects.

Finally while this procedure was developed for sea water samples, it could also be used, with appropriate modifications, for many other environmental samples containing relatively small quantities of stable iodine. We are currently carrying out tests with sediments, corals, rain water, urine, and extremely small quantities of biological or plant material. The case of sediments is particularly interesting. Because of the relatively long residence time of iodine in the ocean, the $^{129}I/^{127}I$ ratio there should be relatively constant. The pre-nuclear ratio is estimated to have been ~1 x 10 ^{12}, which is very close to the pre-nuclear value of the $^{14}C/^{12}C$ ratio in the atmosphere. The machine background of our AMS system is $<10^{-14}$ for $^{129}I/^{127}I$. Thus, using the carrier free procedure described here, it is not unreasonable to imagine dating sediments up to 100 My. Naturally one must still address the question of how constant this ratio has been as a function of time. However, even if this ratio has varied in the ocean, one can envisage calibrating it in the same way that the atmospheric $^{14}C/^{12}C$ ratio has been calibrated.

References

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