

Isotopic signatures: An important tool in today's world

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Abstract

High-sensitivity, high-accuracy actinide measurement techniques developed to support weapons diagnostic capabilities at the Los Alamos National Laboratory are now being used for environmental monitoring. The measurement techniques used are thermal ionization mass spectrometry, alpha spectrometry, and high resolution gamma spectrometry. These techniques are used to address a wide variety of actinide inventory issues; environmental surveillance, site characterizations, food chain member determination, sedimentary records of activities, and treaty compliance concerns. As little as 10 femtograms of plutonium can be detected in samples, and isotopic signatures determined for samples containing sub-100 femtogram amounts. Uranium, present in all environmental samples, can generally yield isotopic signatures of anthropogenic origin when present at the 40 picogram g^{-1} level. Solid samples (soils, sediments, fauna, and tissue) can range from a few particles to several kilograms in size. Water samples can range from a few mL to as much as 200 L.

Introduction

The moratorium on weapons testing has made it necessary to find new applications for the radiochemical diagnostic capabilities of the Chemical Science and Technology Division at Los Alamos. Many were explored, but the three which seemed to hold the highest potential for doing both good science and having sufficient funds to support them were environmental monitoring of actinide elements in support of clean-up efforts, providing tracers for industrial applications, and supporting the International Atomic Energy Agency (IAEA) in its efforts to monitor the Non-Proliferation Treaty (NPT). We are actively involved in the first and third areas and aggressively pursuing the second.

Environmental actinide monitoring has historically been done with inexpensive survey techniques, principally alpha spectrometry (AS). The technique, which is fast and relatively simple, suffers one major drawback; it has inadequate resolution to separate anthropogenic source terms from natural background or fall-out. AS also cannot attribute single versus multiple source terms. Mass spectrometric isotopic dilution (MSID), a tool long used by isotope geologists and the nuclear industry, had not until recently been applied in a broad way to environmental problems. Our first effort using this method was an actinide inventory of the Pajarito Plateau, the area surrounding the Los Alamos National Laboratory (LANL). The method quickly illuminated and expanded the scope of actinides in the environment. Actinide concentrations, previously found to be below health limits and therefore not requiring remedial action or attribution, can now be detected with 100 to 1000 times more

sensitivity than historic techniques and can frequently be attributed to a specific source. While this capability is a powerful new tool for environmental researchers, helping determine transport phenomena and remediation effectiveness, it has also created a communication problem of enormous magnitude. How do you explain to concerned citizens, with little scientific background, the tremendous sensitivity of the method, while assuring them of the corresponding negligible health impact?

The nature of any material processing, including nuclear, causes minute amounts of various constituents to be lost during handling. For example, certain fission products, such as Ru, I, and Tc, have very volatile chemical forms which are difficult to contain. Their detection can provide significant information about the processing nature. The large volume of the material potentially handled by proliferants makes actinides and the associated fission products easy to detect. For this reason, the IAEA has decided to adopt environmental monitoring techniques to assist inspectors in assessing member countries compliance with the NPT and other applicable treaties. A former LANL staff member is in Vienna to help the IAEA build a clean laboratory suitable for environmental measurements. An ongoing program is training chemists and mass spectroscopists from the IAEA in low level environmental measurement techniques. LANL also participated, along with other laboratories, in field trial experiments which were used to demonstrate the merits of the MSID method. LANL is expecting to participate, along with other network laboratories, in the forthcoming environmental monitoring program.

This paper will describe the physical requirements necessary to apply the MSID actinide method at environmental levels, the actinide measurement sensitivities of MSID, and specific applications in various matrices.

Clean chemistry and mass spectrometry

A 1400 m² clean chemistry and mass spectrometry facility was built at Los Alamos to accommodate the processing of samples for weapons diagnostics. This facility permits very small samples of the actinides to be handled such that the integrity of the field sample can be protected from contamination to very low levels. Plutonium process blanks are <3 10⁻¹⁵ grams and uranium blanks <1 10⁻⁹ grams. This facility has the capacity to handle >2000 actinide samples annually at this low blank level. Laminar flow "clean" air passed through hepa-filters directly over work surfaces and rigid protocols for sample content and handling help provide this integrity. A complete description of these techniques can be found in several publications (Efurd *et al.* 1992,1993; Rokop *et al.* 1982).

Because of its high crustal abundance, $\approx 3 \times 10^6$ g g⁻¹, natural U in the environment dilutes anthropogenic source terms and makes U a high accuracy measurement. An anthropogenic source term is detected by slight changes to the 235/238 ratio (natural ratio is 0.007254) and the presence of ²³⁶U. Plutonium, on the other hand, occurs at extremely low concentrations and requires a high-sensitivity measurement. Almost all surface material now contains fallout plutonium in the 10-50 femtogram per ≈ 20 g soil sample range. The 240/239 ratio for fallout is subject to slight changes from local signature overlay. The area near Denver, Colorado, with Rocky Flats providing the local overlay, has a 240/239 fallout ratio of 0.169 ± 0.005 (Efurd *et al.* 1994) while sediment samples collected from the Irish Sea have a 240/239 ratio of 0.24 ± 0.01 (unpublished observations; Efurd *et al.* 1995). The integrated average world-wide ratio is 0.18 (Krey, *et al.* 1976).

Given "clean" chemistry and mass spectrometric capability, there are two different philosophies for making measurements if the goal is detecting undeclared or illicit activity. These are the "bulk" and "particle" methods. The "bulk" method involves total dissolution of the matrix or leaching the desired material from the matrix followed by chemical purification and TIMS. The "particle" method involves collecting particles on swipes or filters, separating the particles and depositing them on a slide with collodian, irradiation in contact with Lexan (for recording the fission tracks created by actinide particles) reregistering the slide and lexan, cutting out the desired particle, and, finally, TIMS. While the "particle" method generates less ambiguous results and has little or no background from natural or fallout sources, it is slow, much more expensive (5x) and highly labor intensive. It also suffers from difficulty at trying to sort out the particular or desired indicator of process. IAEA field trials also demonstrated a lower percentage of "hits" (positive response of anthropogenic origin) than "bulk" (integrated, analysis of entire sample). The best situation would utilize the "bulk" method and if a "hit" was recorded and less ambiguity was desired, this would be followed up with the "particle" method.

As more data is gathered from environmental samples, the question of how to interpret the results is becoming very important. LANL uses algorithms developed for weapons diagnostics to separate multiple actinide sources. We plan to work with the IAEA to refine

these models and make them more useful for their specific purposes.

Table 1 lists a selection of some of the different matrices analyzed by the Chemical Science and Technology Division (Los Alamos National Laboratory) for determining environmental actinides. While this list is incomplete, it serves to indicate the wide application of "bulk" analysis. Particularly effective are filter papers or swipes taken from non-technical areas of nuclear facilities; these give almost complete indication of the process nature.

Table 1

Examples of sample materials for which environmental actinide determinations have been made.

NTS Debris
Soils
Sediments
Sea Water
Fresh Water
Filter Papers
Vegetation
pine needles
grass
apples
feces (sheep)
Soft Tissues
whale liver
whale blubber
star fish
salmon
chubs
trout
Bones

Table 2 shows the measurement sensitivities of the MSID "bulk" analysis method. It can be seen that approximately 1000 times more sample is needed for a signature than is required for detection. A caveat here is that recent chemical purification improvements would indicate a lowering of atoms needed for signature by 10x. A general rule is that the more complicated the matrix is, the more difficult it is to purify the actinide, and, the less sensitive the measurement.

Table 2

Measurement sensitivities for actinides in various matrices and typical sample sizes required for minimum fallout level determinations.

Elemental Concentrations		Isotopic Fingerprints
U	5 x 10 ⁶ atoms	5 x 10 ⁹ atoms
Pu	5 x 10 ⁵ atoms	5 x 10 ⁸ atoms
Am	2 x 10 ⁵ atoms	2 x 10 ⁸ atoms
Np	2 x 10 ⁵ atoms	2 x 10 ⁸ atoms

Sample Matrix	Separation Chemistry Sample Size	% Recovery
Water	2000 ml	>90
Soil	100 g	>90
Biotissue	100 g	>90

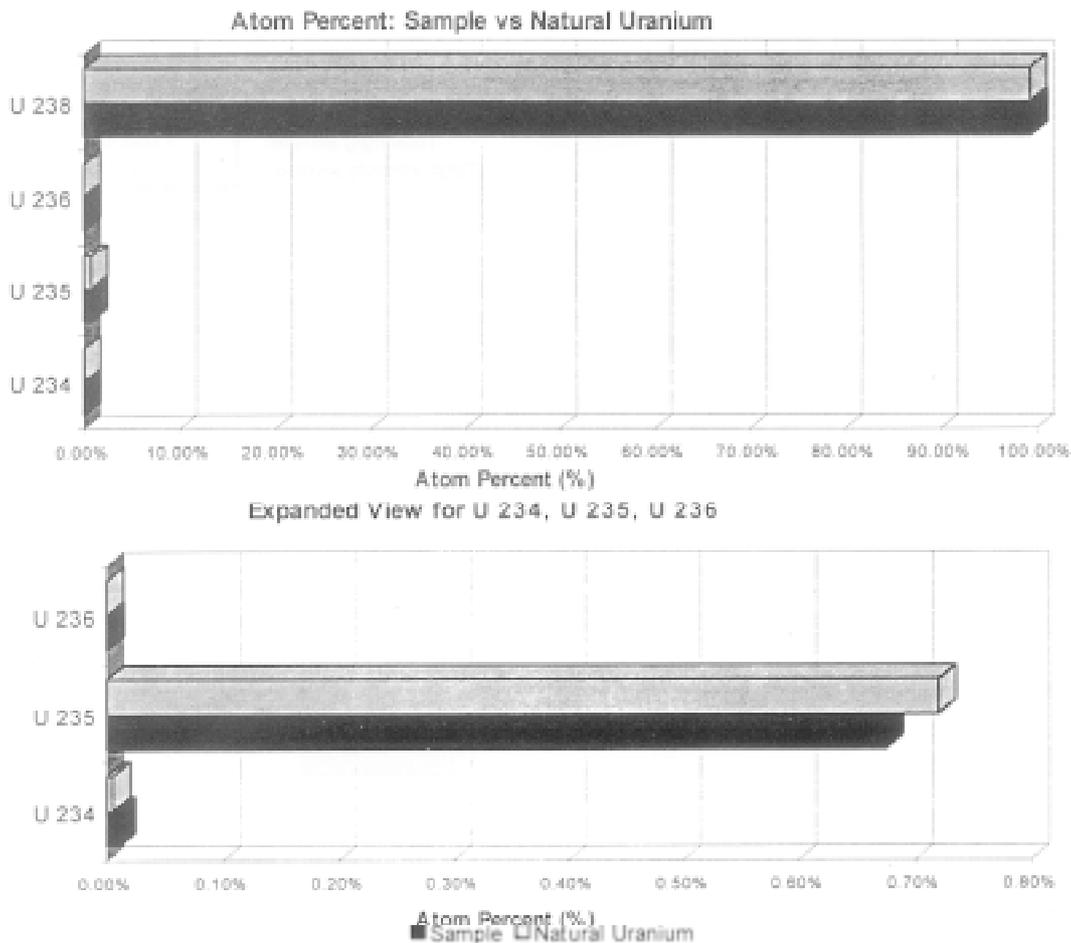
Environmental surveillance, the Pajarito Plateau

In support of the Environmental Surveillance Group at Los Alamos National Laboratory, an actinide inventory of ground waters and sediments from the surrounding Pajarito Plateau was performed. Uranium and plutonium were measured in each sample. Although anthropogenic sources were found for both U and Pu in some samples, no correlation was found between the two. One interesting fact which emerged from the study

was that no modern weapons grade plutonium was found; only pre-1960 material was found. All known sources of plutonium on the plateau were considered; pre-1960 weapons grade ($240/239 \approx 0.01$), modern weapons grade ($240/239 = 0.060 \pm 0.005$), and fallout ($240/239 = 0.18 \pm 0.02$). Only a few samples had modern 240/239 ratios, and they were shown by mixing models to be a mixture of pre-1960s and fallout. This strongly indicates that modern weapons grade material is not present in the samples submitted for analysis.

Isotope	Atom Percent	Concentration atoms/L	Concentration ng/L	Concentration pCi/L	Measurement Error(2σ)
U 234	0.010%	1.69E+ 11	6.58E-02	4.10E-01	8.72E-03
U 235	0.675%	1.12E+ 13	4.36E+ 00	9.42E-03	2.18E-05
U 236	0.000%	4.31E+ 09	1.69E-03	1.09E-04	3.36E-05
U 238	99.315%	1.64E+ 15	6.50E+ 02	2.18E-01	5.39E-04

Total pCi/L sample:	6.38E-01
Error(\pm) in pCi/L:	8.74E-03
Total ng/L sample:	6.54E+ 02
Total atoms/L sample:	1.65E+ 15



- ** The U 236 concentration indicates a neutron radiation history
- ** Comparing the U 235 to natural Uranium indicates that this sample contains a depleted component
- ** The U 234 in this sample is in radioactive dis-equilibrium

Figure 1. Example of a report for uranium analysis (of groundwater); uranium isotopic and activity levels and bar graph representation of field sample in comparison with natural uranium.

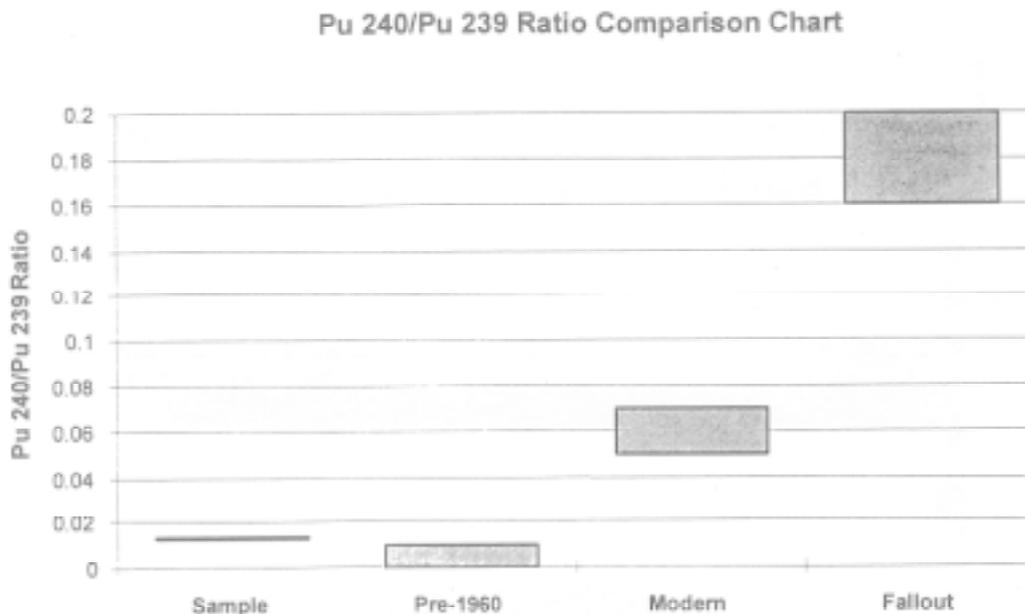
Figure 1 shows a uranium report from this study. The isotopic composition is a mixture of natural uranium, found in all samples as explained above, and depleted uranium. This sample is from groundwater, which is a good medium in which to find an anthropogenic uranium source term as soils and sediments can dilute out unnatural sources very quickly because of their high natural uranium content. A bar graph representation was chosen to compare natural uranium with the isotopic composition found in the sample, to insure that full utilization of the information by a customer with little familiarity with isotopic signatures was possible. Communications with the customer base has become a challenge in itself.

Figure 2 shows a plutonium report from this study. The bar graph shows the three known source terms for the Pajarito Plateau, old pre-1960's Pu, modern Pu, and fallout (see above for isotopic details). This sample is from ≈ 40 grams of sediment obtained from a canyon bottom. The Pu isotopic signature is clearly dominated by the old weapons grade material. This sample has a relatively high concentration of Pu but still shows the effect of mixing with fallout material.

A very accurate history of Los Alamos, at least in its earlier days, could be written from information obtained by environmental monitoring efforts. These efforts also demonstrate the ability to trace a unknown contaminant to its source term.

Isotope	Atom Percent	Concentration atoms/g	Concentration ng/g	Concentration pCi/g	Measurement Error(2 σ)
Pu 239	98.724%	2.56E+10	1.02E-02	6.32E-01	6.95E-04
Pu 240	1.273%	3.31E+08	1.32E-04	2.99E-02	3.64E-04
Pu 241	0.003%	8.82E+05	3.53E-07	3.65E-02	1.65E-02

Total pCi/g sample:	6.98E-01
Error(\pm) in pCi/g:	1.65E-02
Total ng/g sample:	1.03E-02
Total atoms/g sample:	2.60E+10



* Note: Shaded Region Indicates Where Sample Range Must Fall for that Category

Figure 2. Example of a report for plutonium analysis (of sediment); plutonium isotopic and activity levels and 240/239 signature comparison to known source terms on the Pajarito Plateau.

IAEA 93+2 Field trial experiments

The IAEA 93+2 program was started to survey available measurement techniques which could determine compliance of signees to the NPT. The 93+2 program seeks support in;

- a) reliable analytical techniques for the determination of undeclared activities;
- b) training of staff in sampling techniques;
- c) training of staff in selected analytical techniques;
- d) search for and obtain access to environmental data bases; and
- e) to find network laboratories from member states to help relieve the heavy analytical load of the Safeguards Analytical Laboratory (SAL).

The selected techniques should be easily implemented into the IAEA structure and partially supported by member states. The first step in the process is the construction of a "clean" laboratory for the chemical preparation and measurement of environmental samples. The latter task was accomplished with the support of US funds.

The IAEA, with the support the NN-44, the US Department of Energy Office for International Safeguards, conducted a series of field trial experiments at twelve facilities around the world. The experiments were designed to demonstrate whether environmental monitoring could provide evidence of activities conducted within those facilities. These analytical techniques included; radiometric measurements, isotopic measurements by both bulk and particle, accelerator mass spectrometry, and elemental screening. Several laboratories participated, using various analytical techniques. The consensus opinion of the evaluators was that environmental monitoring could, indeed, provide useful evidence. Accordingly, the IAEA board of governors has approved the implementation of environmental monitoring as one means of strengthening safeguards. Of interest to LANL was the fact that actinides, removed from the vicinity of nuclear facilities, in any one of several matrices, could show very clearly the specific activities of that particular facility. Reactors, reprocessing plants, and enrichment plants were monitored.

One item of particular importance emerged; could our QA/QC program (Cappis *et al.* 1994) hold up to the scrutiny of the IAEA if we found evidence of a member states non-compliance with a treaty? We expressed our concern to the IAEA, which was expressing some of the same doubts. This led to confirmation that suitable performance based evaluation standards are not available, so the IAEA initiated a program to produce standards of their own. Our long history of actinide chemistry and measurement will be utilized in this program along with the participation of laboratories in at least three other countries.

Rocky flats environmental monitoring

The Rocky Flats Plant (RFP) near Denver, Colorado, built nuclear weapons components for the USDOE. While the plant was in operation, inadvertent releases of U and Pu occurred. LANL was commissioned to investigate the results of very intense remediation and containment

efforts. Retention ponds, diversion structures, and ditches were used for containment. LANL measured the U and Pu content of waters, soils and sediments over a three year period to determine the success of these efforts.

It should be noted that both inflow and outflow from a creek which passed through the plant boundaries was also monitored. The creek contained fallout Pu and natural uranium coming in to the plant, with slightly reduced concentration of U on the outflow. The outflow did, however, contain an altered isotopic signature from fallout. It should also be noted that the Pu 240/239 ratio characterized for fallout (0.169 versus 0.18), was slightly different from the world integrated average due to local inputs (Efurd *et al.* 1994; Krey *et al.* 1976).

Another observation made during this experiment was that, as expected, anthropogenic U was much more visible in surface waters than in soils or sediments. As pointed out previously, the natural U background in soil quickly dilutes out an anthropogenic source. Pu, however, was more visible in the sediments. There was approximately 50X more Pu in a gram of sediment than in one liter of water (Rokop *et al.* 1994). This is explained by the fact that Pu is adsorbed onto clay particles in the water, which settle as sediments with time. It is unclear whether the Pu is fixed into the sedimentary layers or if it can move from position to position. Experience with sampling from sedimentary clay cores suggests that it stays fixed, at least somewhat, as sedimentary layers from pre-nuclear history, before 1935, do not show Pu from fallout or any other source (Rokop, Efurd, Roensch & Poths, unpublished studies).

While the retention ponds and ditches showed the presence of Rocky Flats product, the remediation efforts were indeed very successful. The concentration of RFP actinides, with one exception, were all far below the very low standards set by the State of Colorado. The one exception, summer-time increase in Pu content of one of the retention ponds, turned out to be due to a near-by volleyball game disturbing soil previously contaminated. This water was retained and remediated until testing demonstrated the removal of Pu. No excursions above, or even close to, Colorado limits were observed outside the plant boundaries.

Conclusion

Isotopic signatures are a powerful tool that can be utilized for a wide variety of new applications. Environmental, industrial, and political spheres will be strongly influenced by their use. This tool is extremely flexible and its use is limited only by imagination.

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