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"ACTINIDE DETERMINATION AND ANALYTICAL SUPPORT FOR CHARACTERIZATION OF ENVIRONMENTAL SAMPLES"

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**ACTINIDE DETERMINATION AND ANALYTICAL SUPPORT FOR
CHARACTERIZATION OF ENVIRONMENTAL SAMPLES**

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ABSTRACT

Clean chemical and Thermal Ionization Mass Spectrometry (TIMS) procedures have been developed to permit the determination of environmental actinide element concentrations and isotopic signatures. The isotopic signatures help identify element origin and separate naturally occurring or background contributions from local anthropogenic sources. Typical sample sizes for processing are 2 liters of water, 1-10 grams of sediment, and 1-20 grams of soil. Measurement limits for Pu, Am, and Np are $< 1 \times 10^8$ atoms, and for U are $< 2.5 \times 10^{12}$ atoms. For isotopic signatures, $< 5 \times 10^8$ atoms of Pu, Am, and Np are necessary, and 8×10^{12} atoms of U are required. Of potential interest to the IAEA is the incorporation of these techniques into their Safeguards Analytical Laboratory for environmental sampling. Studies made of surface waters, sediments and soils from the Rocky Flats Plant (RFP) in Colorado, USA, are used as examples of this methodology. These studies showed that, although plant boundary actinide concentrations approached, on the downstream side, natural or background levels, isotopic signatures characteristic of plant operations were still discernible.

1. INTRODUCTION

The United States underground nuclear weapons test program promoted the development of "clean" chemical and instrumental measurement techniques. These techniques permit the analysis of very small concentrations of actinides extracted from very complex matrices. In support of this mission, Los Alamos National Laboratory built

a special 1400 m² facility that houses "clean" chemical and instrumentation laboratories. "Clean" in this sense means that work surfaces are washed with laminar flow air with fewer than 3500 particles per cubic meter (class-100, < 100 particles/ft³) of 0.5 microns or greater in diameter.

This facility is also being utilized to examine a wide variety of compatible problems which include: determining actinide concentrations and isotopic signatures in surface waters, sediments and soils at the Rocky Flats Plant, CO, USA; determining absolute uranium isotope inventory of holding ponds at the West Valley reprocessing plant, upstate NY, USA; measuring the secular equilibrium concentration of naturally-produced plutonium and technetium in several ore bodies (including Cigar Lake, Canada, and Alligator River, Australia) in support of the International Natural Analogues program; and many isotope geochemistry projects where small, less than picogram or femtogram, amounts of various isotopes (²³⁰Th, ⁹⁹Tc, ²³⁹Pu, ²²⁶Ra, ³He, ²³⁷Np, and noble gas isotopes) are determined. Other projects produce high accuracy determinations of isotopic composition for various elements that are ubiquitous in our environment (Fe, U, Pu, Pb, Nd, Sr, and Ba). To illustrate the use of this facility and the accompanying techniques, results for U and Pu samples taken at RFP will be discussed.

This "clean" facility is unique because of the size of the integrated chemical and instrumental capability under one roof. The methods developed and utilized therein, however, are not restricted to this magnitude of operation. They can be down-sized to much smaller "clean" environments and used to give high-integrity results.

It should be kept in mind that "clean" facilities are designed to deliver analytical results that exactly represent the condition of the "field" sample. If the integrity of analytical results cannot be maintained, proper interpretation of the results is not possible. For this reason, a detailed sampling protocol and performance-based evaluation of an individual laboratory on samples of known composition is the only way to assure that proper interpretations can be made.

2. MEASUREMENT SYSTEM EVALUATION

The methodology used for the chemistry (Efurd, et al.^{1,2}), instrumentation, and mass spectrometry (Rokop, et al.³, Alei, et al.⁴, and Perrin, et al.⁵), is well documented elsewhere.

In order to establish the system accuracy for measuring ratios similar to those expected for environmental samples, synthetic standard solutions were produced from weighed dilutions of well-characterized stock solutions, NBS 949f, a plutonium metal reference standard, and a 99.999% pure ^{242}Pu spike obtained from Lawrence Livermore National Laboratory that was assayed with NBS 949f by isotopic dilution. Sample sizes were varied from 0.1 to 0.5 to 1.0 ng (nominal) to determine the effect of chemical yield on measurement results (see Table (I)). The $^{239}\text{Pu}/^{242}\text{Pu}$ ratios covered the range from $\sim 2.4 \times 10^{-5}$ to $\sim 1 \times 10^{-3}$, for a content of 6.3×10^7 to 2.5×10^9 atoms $^{239}\text{Pu}/\text{sample}$. The results, when obviously contaminated samples are eliminated (5/72 or 6.9 % of the total samples processed), yield positive biases ranging from 21% in the small-value samples to essentially statistical agreement for the more concentrated samples. These positive biases are attributed to the measurement limitations of the single-stage mass spectrometer being used for this experiment. This positive bias represents a 13 fg (3.3×10^7 atoms) equivalent isobar. It should be noted that isotope signatures at the 5×10^8 ^{239}Pu atom level are altered by this level of bias by about 2.5%, about twice the precision / accuracy reported for this measurement. The possibilities of either isobaric interference or contamination at these levels of measurement are very real, even with the "clean" lab. Therefore, the necessity of doing duplicate analyses and frequent parallel blanks is obvious.

System blanks for Pu are $\sim 1 \times 10^7$ atoms and for U, 0.8 to 13×10^{12} atoms. This is the total system blank, including chemistry, loading, and mass spectrometry. The U blank is much higher due to the ubiquitous nature of uranium in our environment.

3. RESULTS AND DISCUSSION

The Rocky Flats Plant Project was initiated to characterize the radioactivity in surface waters and sediments collected at the plant. The study quantified the amount of radioactivity present and determined whether the radioactivity was naturally occurring, background, or a result of plant operations. In this study, the local source terms are well defined, that is, isotope signatures for both uranium and plutonium processed at RFP are a matter of record. The external variables are naturally occurring uranium and its decay products and fallout from weapons testing. Another objective of the study was to identify locations that may contain radioactive sources that could increase surface-water inventories at RFP. The data collected from this study serve as a baseline by which the impact of future remediation efforts can be evaluated.

The Rocky Flats Plant is built on the Eastern slopes of the Rocky Mountains. Prevailing winds blow from West to East and drainage is also from West to East.

The largest amount of anthropogenic activity detected was in the pond sediments. One gram of pond sediment contains about 50 times more plutonium than 1 liter of water (see Table (II)). It is also apparent that both depleted uranium and plutonium are mobile through the drainage system. The largest source of activity, however, is naturally occurring uranium and its decay product radium, which provides 70 to 450 times more alpha activity than that produced by the plutonium in the terminal ponds. The largest source of anthropogenic activity was depleted uranium that comprised 20 to 50% of the total alpha activity in the sample.

Samples taken upwind and upflow (outside the plant boundaries) showed only naturally occurring U. Pu concentration was found at fallout levels with the $^{240}\text{Pu}/^{239}\text{Pu}$ ratio also reflecting fallout.

3.1. Plutonium Results

Table (II) shows a small sample of the results from the measurement of the concentration and isotopic signature of plutonium from several of the holding ponds and sediments at the Rocky Flats Plant. Plutonium concentrations vary from 0.13 to 27.12×10^9 atoms per liter, a factor of ~200, with the measured isotopic signature maintained within measurement error over the entire range. Smaller concentrations of Pu were measured in water, but isotope signatures were not obtainable. The sediment samples in Table (II) show much higher concentrations of Pu, approximately 50 times, and the $^{240}/^{239}\text{Pu}$ ratios are high precision measurements, with the exception of A-1, where low count rates yielded a poor result. With only four exceptions, the Pu concentrations measured in the waters around RFP were below allowable discharge limits, but still permitted the identification of the source term by isotopic signature. Concentrations were determined by mass spectrometric isotope dilution.

Three terminal holding ponds, A-4, B-5, C-2, and the sewage treatment plant were monitored on a monthly basis (see Figure (1)). The Pu concentration of pond C-2 definitely increases during the warmer months and may be caused by increased biologic activity (algae growth), increased solubility due to higher temperatures, or simply physical disturbance by plant personal. An experiment planned to identify the cause of this increased concentration would be of benefit for future sampling strategies.

If a more sensitive measure of local activity and/or a time record is desired, sediments, where the Pu is more concentrated, are the samples of choice. These layers could, therefore, provide a history, for an extended period, of declared / undeclared activity levels determined from plutonium concentrations with isotope signatures providing source term identification. Other elements found in waters and sediments, such as technetium⁶, could provide additional information.

3.2. Uranium Results

Uranium is quite different from plutonium in that it is relatively abundant in nature, as much as 3.5 ppm in most regions of the earth's crust, and even higher in areas where uraniferous ores are present. For this reason, it is much more difficult to detect anthropogenic U contamination. While a change in ratio of the major isotopes, ^{235}U and ^{238}U , whose relative natural abundance is $\sim 1/137.8$, provides the best chance of determining anthropogenic activity, high concentration of these isotopes can mask the presence of other isotopic compositions of uranium. Uranium, however, has two other long-lived isotopes, ^{234}U and ^{236}U . Uranium-236 is generated by neutron capture on ^{235}U , and is present in almost all anthropogenic uranium associated with nuclear fuel or weapons materials. In addition, ^{234}U , ~ 55 ppm of natural uranium, also has its' composition changed when either depleted or enriched material is added to that which occurs naturally. These two isotopes, therefore, present two additional chances for detecting the presence of anthropogenic insertions into the environment.

Table (III) shows a sample of some of the uranium measurements made in several ponds, sediments, and a ditch at the Rocky Flats Plant. The range of concentrations is much smaller, $\sim 30x$ versus $\sim 200x$, than in the case of plutonium because of the considerable background of natural uranium. Pond C-1 shows a near-natural composition of uranium while pond A-1 closely approaches depleted uranium values. The ^{236}U content of pond A-1 also shows considerable increase over zero natural content giving additional evidence of the presence of anthropogenic uranium. Pond A-3, while closely approaching a natural $^{235}\text{U}/^{238}\text{U}$ ratio, has perturbed ^{234}U and ^{236}U content showing an anthropogenic contaminant. The ponds on the downstream side of RFP show very low natural concentrations of U, but the isotope signatures indicate perturbed ^{234}U and ^{236}U contents. Measurements of this type would be useful for detecting possible proliferant activities.

It has become apparent, during the course of making measurements at RFP, that two different types of analyses are required; the Pu, which has a very low concentration in nature, due to fallout, remains a high-sensitivity relatively low-precision measurement, while U, because of its abundant concentration in the earth's crust, has become a high-precision high-accuracy measurement requiring the accurate measurement of the low-abundance isotopes ^{234}U and ^{236}U .

3.3. Discussion

The combination of clean room chemistry and TIMS is a very sensitive, specific, and unambiguous method for the determination of very low levels of actinides in environmental samples. Source term identification information provided by isotopic signatures also helps separate anthropogenic from natural components. The ability to isolate and characterize even very small quantities of actinides from large volumes of complex matrices permits the detection of undeclared activity with a very high success rate. Once the activity has been discovered, a whole barrage of other more specific analyses, including particle analysis, can be brought to bear on the problem. This integrated sample approach, which was developed at LANL for nuclear weapons testing, provides the non-proliferation and counterproliferation community a unique and cost effective tool.

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TABLE I. PLUTONIUM BLEND DATA - MEASURED $^{239}/^{242}\text{Pu}$ RATIOS

| ng Pu Loaded | Blend 1 | Blend 2 | Blend 3 | Blend 4 |
|-------------------------|---------------------|--------------------|--------------------|--------------------|
| 0.1 | 0.000031 | 0.000249 | 0.000496 | 0.000978 |
| | *0.000143 | 0.000249 | 0.000487 | 0.000982 |
| | 0.000025 | 0.000254 | 0.000507 | 0.000989 |
| | 0.000027 | 0.000247 | 0.000502 | *0.000958 |
| | 0.000026 | 0.000255 | 0.000494 | 0.000993 |
| | 0.000023 | 0.000251 | *0.000552 | 0.000997 |
| Mean | 0.000026 | 0.000251 | 0.000497 | 0.000988 |
| SD | 0.000003 | 0.000003 | 0.000008 | 0.000008 |
| 0.50 | 0.000032 | 0.000248 | 0.000524 | 0.000998 |
| | 0.000028 | 0.000255 | 0.000513 | 0.000972 |
| | 0.000034 | 0.000244 | 0.000505 | 0.001009 |
| | 0.000034 | 0.000265 | 0.000506 | 0.001003 |
| | 0.000035 | 0.000248 | 0.000492 | 0.000989 |
| | 0.000030 | 0.000260 | 0.000513 | 0.000974 |
| Mean | 0.000032 | 0.000253 | 0.000509 | 0.000991 |
| SD | 0.000003 | 0.000008 | 0.000011 | 0.000015 |
| 1.0 | 0.000027 | 0.000248 | 0.000491 | 0.000996 |
| | 0.000028 | 0.000249 | 0.000491 | 0.000995 |
| | 0.000027 | 0.000254 | 0.000501 | 0.001001 |
| | *0.000096 | 0.000249 | 0.000509 | *0.001026 |
| | 0.000028 | 0.000250 | 0.000494 | 0.000992 |
| | 0.000029 | 0.000244 | 0.000510 | 0.001005 |
| Mean | 0.000028 | 0.000249 | 0.000499 | 0.000998 |
| SD | 0.000001 | 0.000003 | 0.000009 | 0.000005 |
| Overall Mean | 0.000029 | 0.000251 | 0.000502 | 0.000992 |
| SD | 0.000003 (11.8%) | 0.000005 (2.1%) | 0.000010 (2.0%) | 0.000011 (1.1%) |
| Make Up Value | 0.000024 | 0.000247 | 0.000496 | 0.000995 |
| Bias from Make Up Value | +21% | +1.6% | +1.3% | -0.3% |

*Contaminated in process, dropped from mean and standard deviation (SD)

TABLE II. PLUTONIUM CONCENTRATIONS AND $^{240}/^{239}\text{Pu}$ ATOM RATIOS FROM SURFACE WATERS AND SEDIMENTS AT RFP

| WATERS | | | | | |
|--------------|------|---------------|-----------------------|--|-------|
| Date Sampled | Pond | Sample Number | Atoms/L x 10^{-9} * | Atom Ratios $^{240}/^{239}\text{Pu} \pm 1$ Sigma | |
| 02/24/93 | A1 | SW60312WC | 2.36 | 0.054 | 0.004 |
| 05/12/93 | A1 | SW60017JE | 0.55 | 0.063 | 0.009 |
| 08/24/93 | A1 | SW60051JE | 1.08 | 0.055 | 0.005 |
| 11/25/92 | A2 | SW60294WC | 27.12 | 0.064 | 0.007 |
| 02/24/93 | A2 | SW60311WC | 1.06 | 0.058 | 0.010 |
| 05/12/93 | A2 | SW60016JE | 0.13 | 0.055 | 0.008 |
| 05/12/93 | A3 | SW60015JE | 0.15 | 0.059 | 0.005 |
| 02/24/93 | B4 | SW60314WC | 3.21 | 0.066 | 0.008 |
| 05/13/93 | B4 | SW60020JE | 1.45 | 0.059 | 0.007 |
| 08/24/93 | B4 | SW60045JE | 1.92 | 0.060 | 0.005 |
| 02/23/93 | C1 | SW60320WC | 0.35 | 0.064 | 0.009 |
| 05/13/93 | C1 | SW60025JE | 0.30 | 0.069 | 0.006 |
| 08/23/93 | C1 | SW60050JE | 2.34 | 0.057 | 0.005 |
| SEDIMENTS | | | Atoms/g x 10^{-9} | | |
| | A1 | SW60277WC | 98.0 | 0.052 | 0.005 |
| | A2 | SW60285WC | 116.8 | 0.061 | 0.001 |
| | B4 | SW60272WC | 43.8 | 0.059 | 0.001 |

*Two liters of water processed per sample.

TABLE III. URANIUM CONCENTRATIONS AND ISOTOPIC COMPOSITIONS FROM
SEDIMENTS, SOILS AND WATERS

| SEDIMENTS AND SOILS | | Uranium Atom Percent | | | | Atoms/g x 10 ⁻¹⁵ |
|------------------------|--------------------------|----------------------|--------|--------|---------|--------------------------------|
| Sample Number | Description | U-234 | U-235 | U-236 | U-238 | |
| | Natural U | 0.0057 | 0.7204 | 0.0000 | 99.2739 | |
| SW60038JE | A-1 Bypass S* | 0.0056 | 0.6483 | 0.0009 | 99.3452 | 7.03 |
| SW60277WC | A-1 Pond S* | 0.0025 | 0.3571 | 0.0024 | 99.6380 | 16.31 |
| SW60285WC | A-2 Pond S* | 0.0026 | 0.4017 | 0.0023 | 99.5933 | 22.60 |
| SW60270WC | A-3 Pond S* | 0.0048 | 0.6383 | 0.0009 | 99.3561 | 6.30 |
| SW60268WC | A-4 Pond S* | 0.0047 | 0.6183 | 0.0008 | 99.3763 | 4.40 |
| SW60026JE | C-1 Pond S* | 0.0055 | 0.7166 | 0.0000 | 99.2779 | 2.17 |
| SW60004JE | SID+ Soil | 0.0044 | 0.5614 | 0.0016 | 99.4325 | 4.30 |
| SW60009JE | SID+ Soil | 0.0063 | 0.7166 | 0.0000 | 99.2771 | 1.79 |
| SW60041JE | SID+ Soil | 0.0040 | 0.5067 | 0.0019 | 99.4873 | 9.57 |
| WATERS | | | | | | Atoms/L x 10 ⁻¹⁵ |
| SW60312WC | A-1 Pond (2) | 0.0040 | 0.7138 | 0.0020 | 99.2802 | 2.73 |
| SW60051JE | B-1 Pond (8) | 0.0052 | 0.4339 | 0.0020 | 99.5589 | 59.44 |
| SW60297WC | B-2 Pond (11) | 0.0068 | 0.7225 | 0.0014 | 99.2693 | 26.13 |
| *Sediment | +South Interceptor Ditch | | | | | |

Figure 1
Plutonium Concentrations in Locations Analyzed Monthly

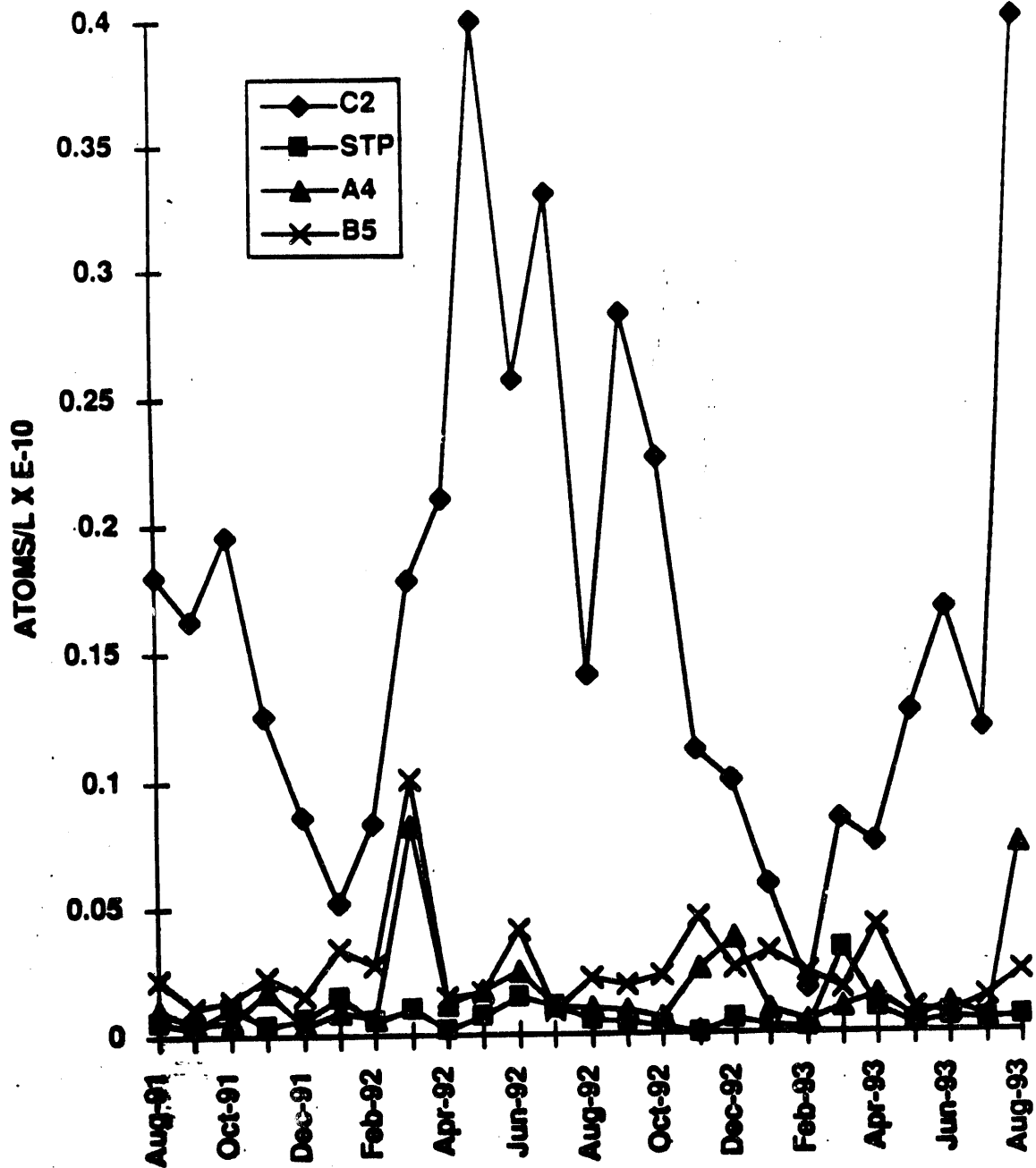


Figure 1: Plutonium concentrations for terminal ponds A-4, B-5, C-2, and sewage treatment plant (STP) as a function of time.

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