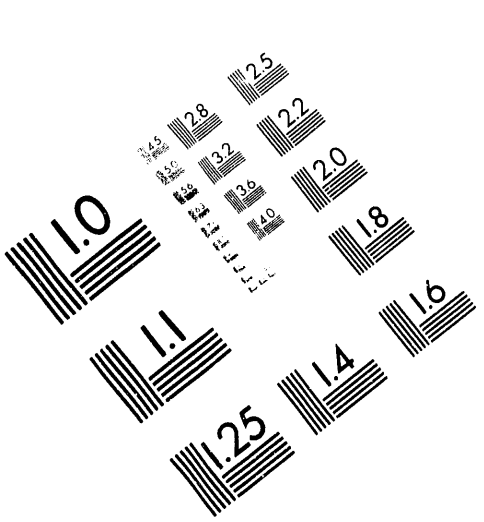

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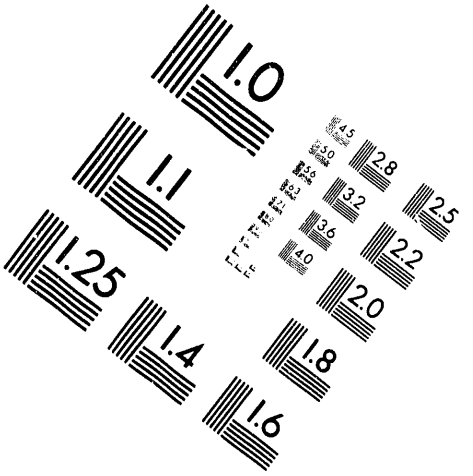

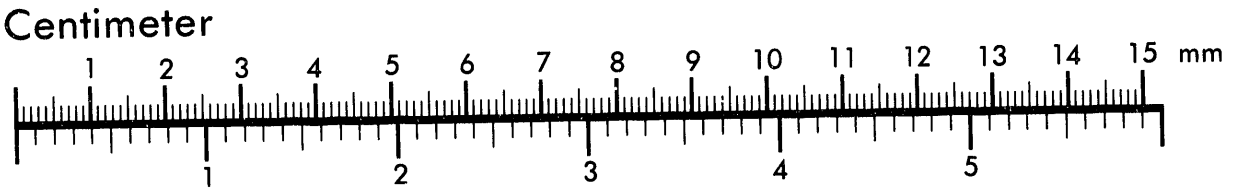

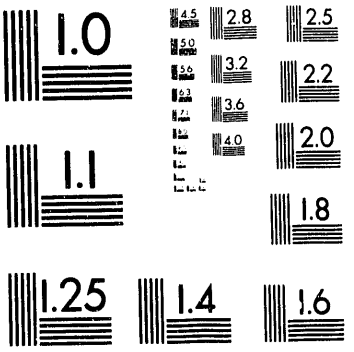

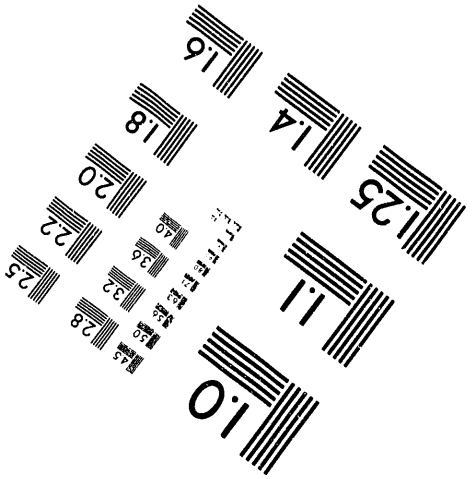

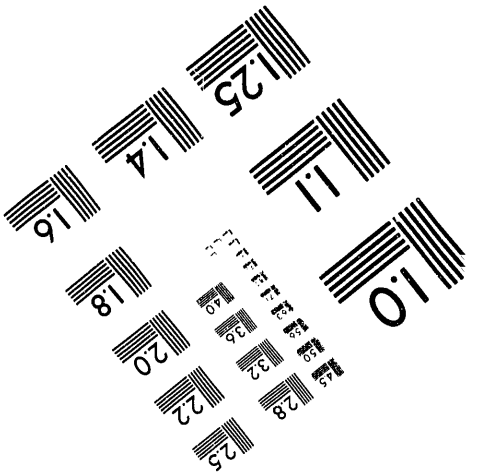

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PLUTONIUM BIOASSAY BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP/MS)

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PLUTONIUM BIOASSAY BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP/MS). E.J. Wyse and D.R. Fisher (Pacific Northwest Laboratory*, P.O. Box 999, Richland, WA 99352)

ABSTRACT

The determination of plutonium in urine poses several analytical challenges, e.g., detectability, matrix, etc. We have investigated the feasibility of analyzing plutonium in processed urine by inductively coupled plasma mass spectrometry (ICP/MS). The urine samples are first spiked with ^{244}Pu as a tracer and internal standard, then processed by co-precipitation and column chromatography using TRU-Spec™, an extraction resin. By enhancing ICP/MS detection capabilities via improved sample introduction and data acquisition efficiencies, an instrumental detection limit of 5 to 50 fg (0.3 to 3 fCi for ^{239}Pu) is typically obtained, depending on the desired degree of quantitation.

A brief summary of the analytical method as well as the basis for measuring radionuclides by ICP/MS are submitted; the separation procedure, methods of sample introduction, and data acquisition techniques are then highlighted.

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INTRODUCTION

Inductively Coupled Plasma Mass Spectrometry (ICP/MS) Overview

Mass spectrometry is not a novel technique for certain radioanalytical applications. Its superb sensitivity, excellent precision, and isotopic analysis capabilities contribute to making mass spectrometry a useful tool for measuring many radionuclides that would otherwise be difficult to determine using decay counting techniques. What has made conventional mass spectrometry (as well as decay counting) unfeasible in the past for large-scale sample analyses, however, is its extremely low sample processing rate. Laborious sample preparation required for thermal ionization mass spectrometry (TIMS) and long analysis times permit only a few samples to be processed and analyzed per day. This rate is far too inefficient for many environmental and biological studies that may require hundreds to thousands of samples to be analyzed, as well as for those which require results reported in a timely manner.

The ICP/MS technique was introduced to the commercial market in 1983 by VG Instruments of the United Kingdom, manufacturer of the PlasmaQuad. A unique sample interface utilizing stepwise pressure reduction integrates an inductively-coupled plasma as an ion source with a quadrupole mass spectrometer. The result is an analytical instrument that combines the advantages of conventional MS (described above) with the relative ease and high sample processing rate of ICP optical emission spectrometry (OES). Most aqueous samples can be aspirated directly into the plasma, thereby circumventing much of the tedious sample preparation necessary in processing samples for conventional mass spectrometric analysis. Exceptional sensitivity allows a data acquisition time of less than 1 min/sample to be sufficient for adequate counting statistics; newer instruments with standard equipment have a typical response on the order of over 10 million counts/sec/ppm with a background count rate of approximately 10 counts/sec.

Basis for Measuring Long-Lived Radionuclides by ICP/MS

A radionuclide is traditionally measured by instrumentation that detects and/or analyzes the radiation emitted during the nuclide's decay. While decay counting or energy emission spectrometry is often adequate for radionuclide analysis, limitations imposed by certain physical properties of radioactive decay (e.g., the type and energy of radiation emitted, the radionuclide's specific activity, and the branching fraction of the energy emitted) may make it impractical or impossible to measure a nuclide by analyzing its decay. Instrumental limitations and the necessity of using more than one radiation spectrometry technique for analyzing multiple radionuclides can also make decay analysis unfeasible.

Because it detects atoms rather than energy emissions, ICP/MS is not limited by physical properties of radioactive decay. The detectability of an isotope by ICP/MS is instead primarily a function of the quantity of that isotope's atoms present. For a given activity, the quantity of atoms increases with increasing half-life. This is illustrated in the equation

$$\mathbf{A = \lambda N} \qquad (1)$$

where A = activity

$\lambda = \ln 2 /$ half-life

N = number of atoms

As the half-life approaches infinity, ICP/MS has a significant advantage over decay analysis because the atoms are present, but the activity is not. A conservative estimate of the minimum half-life that a radionuclide must have for detection by ICP/MS in a matrix-free "environmental" sample (i.e., the total sample activity is <100 dpm) is ~10^3 years.[1,2] If the ICP/MS is shielded to accommodate radioactive samples, the environmental activity parameter is not required, and measurement is possible for nuclides with much shorter half-lives.

ICP/MS Sample Introduction

Just as the original ICP/MS combined two established analytical techniques (ICP-OES and TIMS) to make an original analytical technique with superior capabilities, two established methods of sample introduction have recently been interfaced with an ICP/MS, each of which has demonstrated impressive results. Electrothermal vaporization (ETV) and ultrasonic nebulization (USN) have been previously used with other analytical techniques, and both provide dramatically improved sample transport efficiency to the ICP, resulting in significantly better overall sensitivity and analyte detectability.

For sample atomization, ETV employs a graphite furnace similar to that used in flameless atomic absorption. The initial removal of sample moisture and a sample transport efficiency believed to be close to 100% give ETV the lowest absolute detection limits ever observed for ICP/MS (<10 fg, or ~1 x 10^8 atoms, by single ion monitoring — see Figure 1). Because it is restricted to sample sizes less than 100 mg, ETV is ideal for small sample quantities; unfortunately, this restriction greatly limits the ETV capability. Other limitations include matrix sensitivity (the instrument response is substantially diminished when analyzing samples with matrices containing total dissolved solids >100-1000 ppm), the inability to measure other isotopes in its most sensitive mode (single ion monitoring), and relatively poor precision and reliability (see Figure 2).

Ultrasonic nebulization has been previously used for ICP-OES with limited success. "Homemade" USN's tested 15 to 20 years ago provided memory effects and overall instability. Doubts regarding USN as a reliable method of sample introduction persisted, and improvements were not pursued. Recently, however, Cetac of Omaha, Nebraska, has developed an instrument that overcomes most of the initial criticisms associated with USN. The instrument first generates a thick, dense aerosol using an ultrasonic transducer. The aerosol is then desolvated before being introduced into the plasma. The result is a "dry" sample aerosol with a sample introduction efficiency on the order of ~15%, compared to 1 to 2% for pneumatic nebulization. Signal stability and overall reliability is comparable to that of pneumatic nebulization, and instrument response is improved by a factor of 10 to 50X. Because USN does not require single ion monitoring (SIM) for optimal performance, scanning or peak hopping is the usual mode of data acquisition, allowing the measurement of additional isotopes. As with ETV, analysis using USN is more sensitive to high dissolved solids matrices than is pneumatic nebulization.

Data Acquisition

Three modes of data acquisition are used in ICP/MS analysis. In scanning mode, a defined mass range is examined via a multi-channel analyzer, and the result is a mass spectrum (see Figures 3A and 3B). In single ion monitoring (SIM) mode, the response for only one selected atomic mass unit (amu) is recorded over time, and the result is a time-resolved spectrum (Figure 1). Peak hopping (or peak jumping) mode implements aspects of both scanning and SIM. After the desired peak width has been identified, the quadrupole scans only the *peaks* of the selected isotopes; this results in maximizing data acquisition time for the isotopes of interest while minimizing total acquisition time (a few

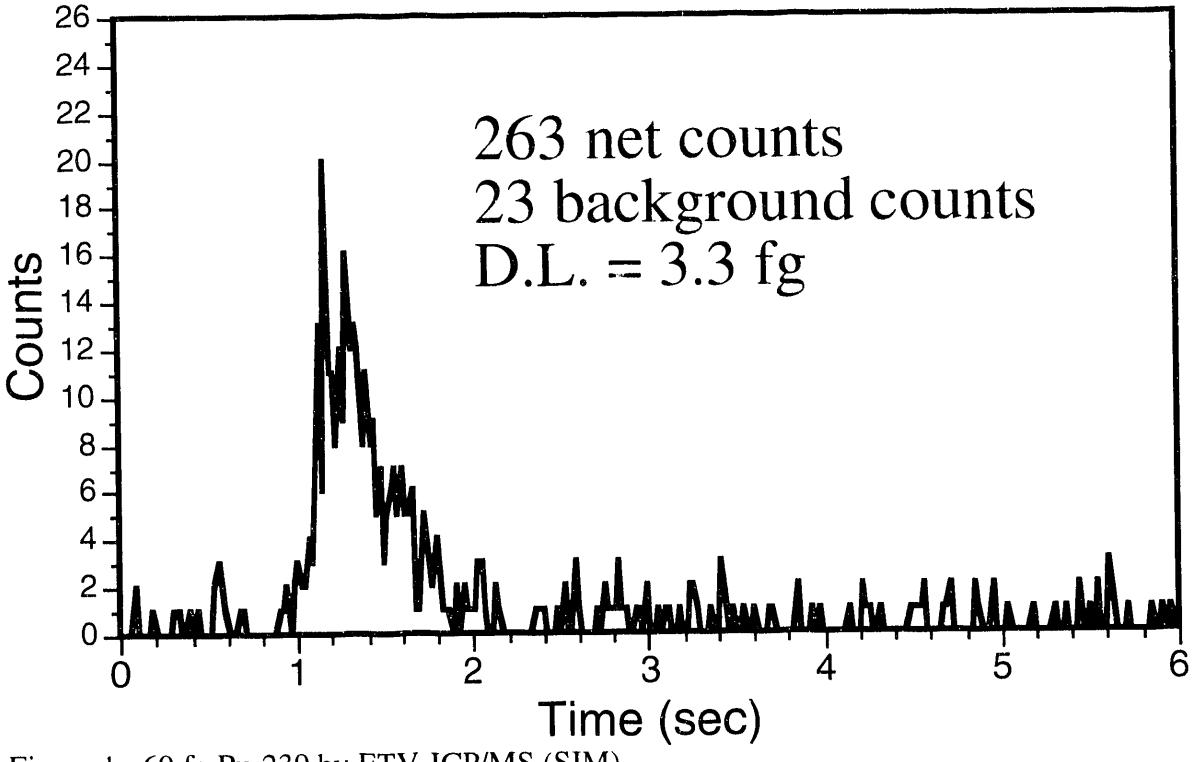


Figure 1. 60 fg Pu-239 by ETV-ICP/MS (SIM)

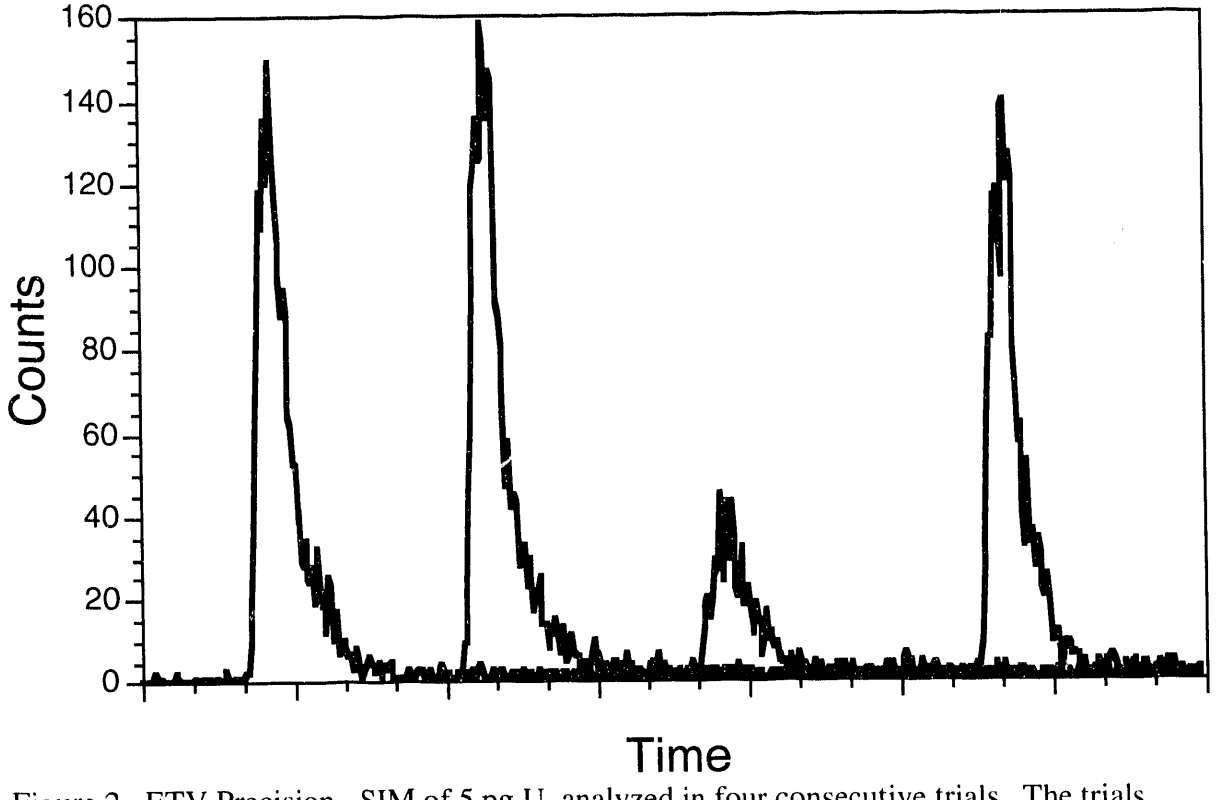
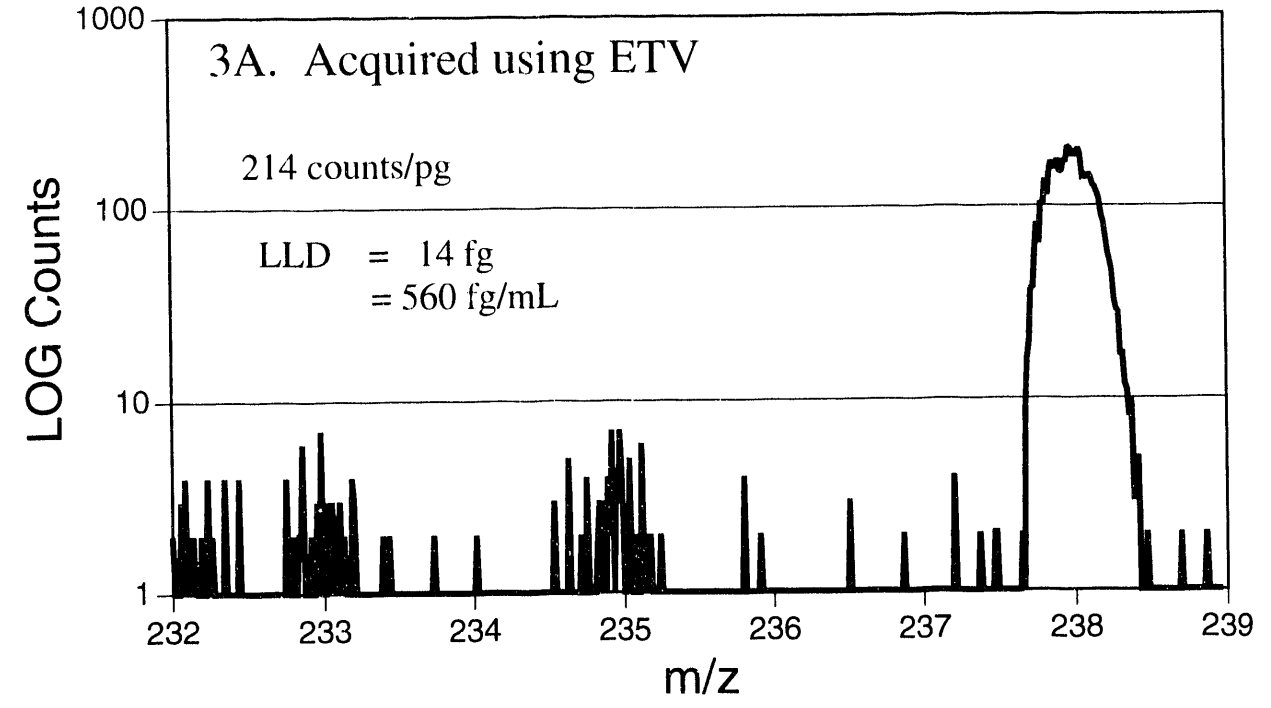
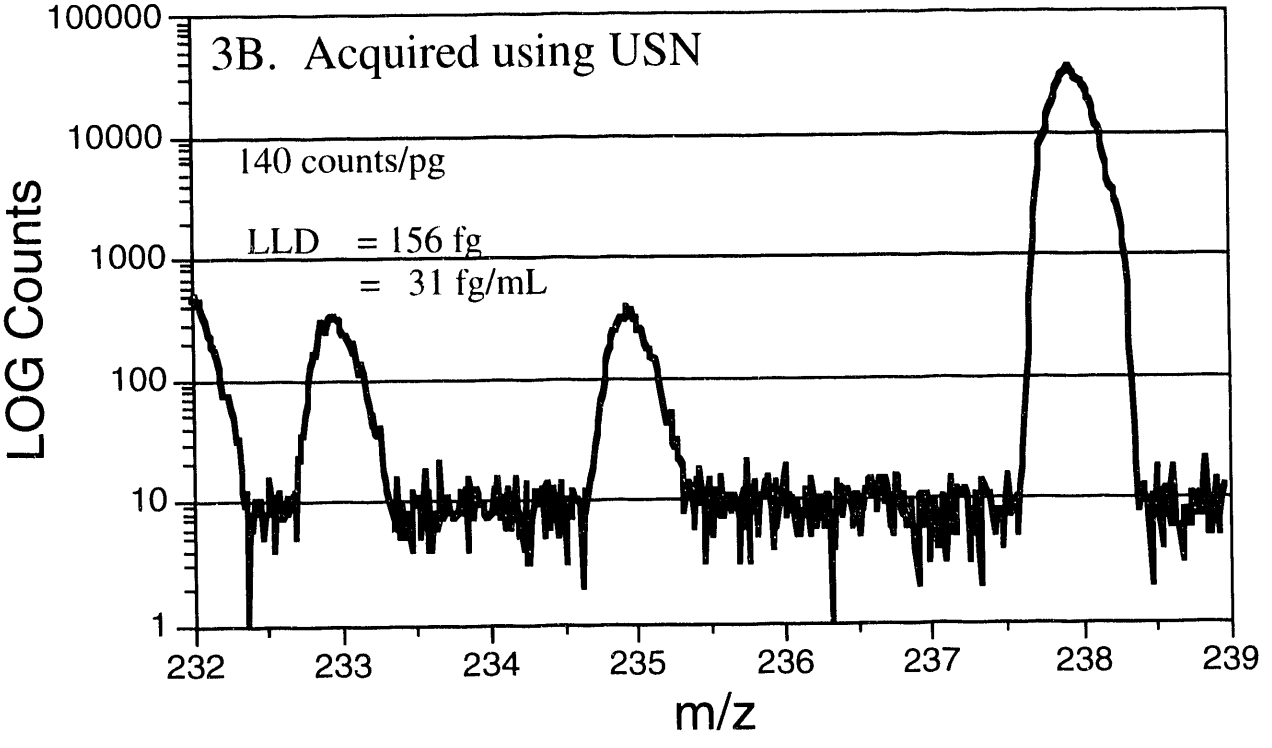


Figure 2. ETV Precision. SIM of 5 pg U, analyzed in four consecutive trials. The trials were performed over the course of ~30 min; peak width is ~1 sec. (X-axis is not to scale.)





Figures 3A & 3B. Analysis of 1 ppb U Isotopic Standard (233:235:238 = 1:1:100) by ETV- and USN- ICP/MS

seconds is typically adequate). The resulting data are not a mass spectrum, but rather consecutive step functions representing the peak centroid and designated adjacent channels. The peaks are ordered by increasing mass, but are not separated by mass units; i.e., if the peak-hopping procedure included 239 and 244 amu, the peaks would be adjacent to each other rather than separated by 5 amu. This is illustrated in Figure 4; however, a small space was inserted between peaks to facilitate their identification. (A background response is typically established by including an amu that should not have a response; for this study, 246 amu was chosen as an appropriate background.)

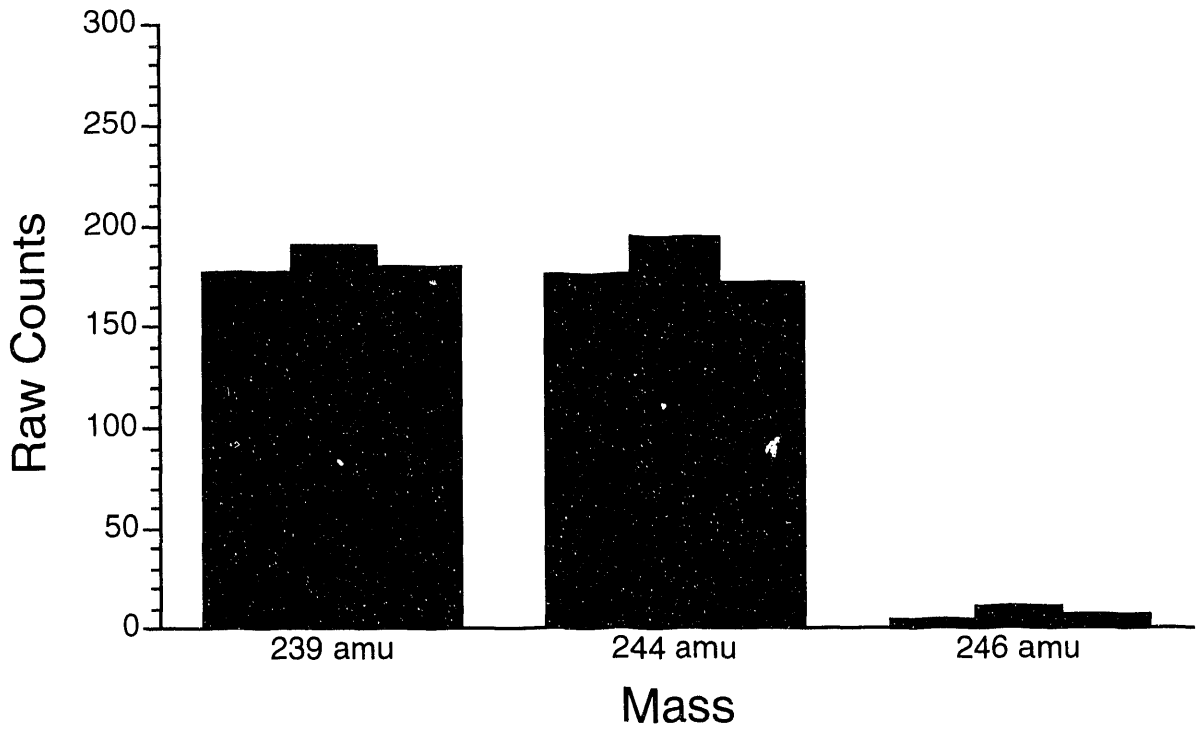


Figure 4. Peak-Hopping Spectrum

EXPERIMENTAL

To obtain the maximum sensitivity in a high-solids organic matrix, a separation procedure is necessary. The following co-precipitation separation procedure is similar to that used for alpha spectrometry:[a]

1. The urine sample volume is measured using an appropriately sized Class A certified graduated cylinder. The sample is then transferred to a 500 mL (or larger, if necessary) beaker containing a stirring bar.

2. Approximately 100 pg of ^{244}Pu is added to the sample. (The ^{244}Pu will act as both a tracer to normalize for analyte recovery and an internal standard to normalize for instrument drift during analysis. All blanks and standards are spiked with the same concentration of ^{244}Pu as should be in the final sample, assuming 100% recovery; concentration = quantity spiked / final volume of sample before analysis.)

3. The sample is placed on a magnetic stirrer hot plate. Two drops of 2-octanol (to control foaming), 30 mL concentrated HNO_3 and 0.5 mL of a 5% Ca (carrier) solution are added to the sample. The sample is then stirred for 5 min before being heated at 90°C for 2 h.

4. After cooling for ~15 minutes, 2.5 mL of a 30% phosphate solution is added to the sample solution. The precipitate is then formed by adding 50 mL concentrated ammonium hydroxide and stirring for 5 min. After the solution has completely cooled, an additional 0.5 mL of the Ca solution is stirred in, and the precipitate is allowed to settle for 1 h. (Separation column may prepared at this time — see step 8.)

5. After decanting the sample solution, the precipitate is transferred to a 50 mL centrifuge tube and spun for 5 to 20 min until a clear supernate is obtained. The supernate is decanted and discarded.

6. The precipitate is dissolved in 10 mL concentrated HNO_3, and transferred back to the original beaker. The tube is rinsed with two 5 mL aliquots of concentrated HNO_3, and each rinse is added to the sample.

7. The sample is brought to a white ash by boiling with 2 to 3 mL hydrogen peroxide and taking almost to dryness. (Baking the sample should be avoided, as it may cause the Pu species to become refractory.) The ashing cycle is repeated with 2 mL HNO_3 and 1 mL hydrogen peroxide until the material is almost pure white (2 to 5 times). The residue is dissolved in 10 mL 2M HNO_3.

8. A separation column is prepared by adding approximately 1 mL TRU-Spec™ resin (EIChroM Industries) to a 5 mL disposable column. The column is rinsed with 20 mL deionized water followed by 20 mL 2M HNO_3.

9. The dissolved residue is passed through the prepared column at a rate of approximately 1 mL/min. The column is then rinsed with 10 mL 1M HNO_3.

10. The column is eluted with 15 mL 0.05M ammonium bioxalate, and the eluant is collected in a 30 mL Pyrex beaker.

11. The eluant beaker is placed on a hot plate, where the eluant is taken to dryness. The residue is dissolved in 0.5 mL 0.5M HNO_3, scraping the beaker bottom with a plastic pipet tip to free any refractory Pu. The final sample is then analyzed by ICP/MS using both ETV and USN as methods of sample introduction.

RESULTS AND DISCUSSION

In initial experiments, the eluant was reduced to a volume of ~0.5 mL via evaporation without first taking it to dryness. The problem with this practice was obtaining satisfactory analyte recovery without recrystalizing the oxalate matrix. It was found that at lower eluant concentrations (~0.01M oxalic acid), recrystalization during volume reduction was not a problem; unfortunately, this concentration was insufficient to effectively elute the Pu. When the eluant concentration was increased and the volume (after eluting) was reduced from 15 mL to less than one mL, the oxalate would recrystalize upon cooling. Eluting with 0.05M oxalic acid, evaporating the eluant to

dryness and dissolving the residue in 0.5M HNO_3, resulted in virtually eliminating the precipitate while attaining acceptable analyte recovery (50 to 90+%).

Although the ultimate detectability for Pu by ICP/MS had been attained via ETV in previous and preliminary experiments, it became apparent that sensitivity would have to be compromised for precision, multi-isotope capabilities, and most importantly, reliability. The ETV technique showed such promise for absolute detectability in initial experiments that it was difficult to abandon; the goal of the study was to attain low femtogram detection limits in urine, and that level of detection was being attained in deionized water by ETV (illustrated in Figure 1). Acceptable performance was erratic, however: sometimes the ICP/MS was responsive to the ETV, sometimes it was not. While such conflicts could often be resolved, it was usually at the expense of both time and reasonable performance. Even when the performance was acceptable, overall precision between standards in a dilute HNO_3 matrix was inferior to nebulization. When sample matrices other than deionized water or dilute HNO_3 were processed by ETV (e.g., the sample eluant), performance was consistently poor. In addition, optimal detection could only be achieved in SIM mode; the transient signal resulting from an ETV burn required a "captive audience" for complete detection. Proper quantitation required the measurement of at least a tracer, an internal standard, and a background mass, but distributing data acquisition time between multiple isotopes significantly impeded performance. For these reasons, focus was eventually turned to ultrasonic nebulization as the method of sample introduction for this study.

It was found that while absolute detectability in terms of quantity (i.e., femtograms) was theoretically superior by ETV, detectability in terms of concentration (i.e., quantity per volume) was superior by USN. Because USN is not limited to 0.1 g of material (as is ETV), a greater sample quantity (and thus more atoms) can be introduced via USN. This is best illustrated in Figures 3A and 3B. In a separate experiment, an isotopic solution of ^{233}U, ^{235}U, and ^{238}U (concentration ratio = 1:1:100, respectively) at a concentration of 1 ppb ^{238}U was analyzed by both techniques. For ETV, 25 µL was loaded onto the furnace for analysis, and for USN, a 5 mL sample was completely aspirated in the course of ~5 min. Although the detection limit using ETV was only 14 fg, the peak shapes and response were far better using the USN because a greater volume of sample was introduced. For the purposes of the Pu separation study, all of the final sample volume can be aspirated by USN, compared to only 10 to 20% of the final sample volume burned for a given ETV run.

Changing the data acquisition mode from scanning to peak hopping resulted in better absolute detection limits. Parameters were optimized so that a maximum amount of time could be spent exclusively on ^{239}Pu, ^{244}Pu; a background response was obtained at 246 amu (see Figure 4). Acquiring data in this manner proved to be effective; a detection limit of 0.1 pg/mL (ppt) could be obtained on a volume as little as 0.5 mL (50 fg). Peak hopping also provided outstanding precision and accuracy; a calibration curve for a 1 mL analysis on standards ranging in concentration from 0.5 ppt to 20 ppt is depicted in Figure 5.

POSSIBLE AREAS OF IMPROVEMENT

As sensitive as it is, ICP/MS is relatively inefficient in transporting sample to the detector. For this reason and others, there is ample room for improving the ultimate detection capability of ICP/MS.

Some improvement has recently been made (and has been implemented on newer-model ICP/MS units) in the ion transport efficiency of the sample interface, one of the primary areas for ion loss. (The sample interface is where the ions move from atmospheric pressure to an area of reduced pressure.) This has resulted in a 2 to 5X

improvement in instrument response over older models. While this is a significant improvement, it is conceivable that far better efficiency can be attained through further development.

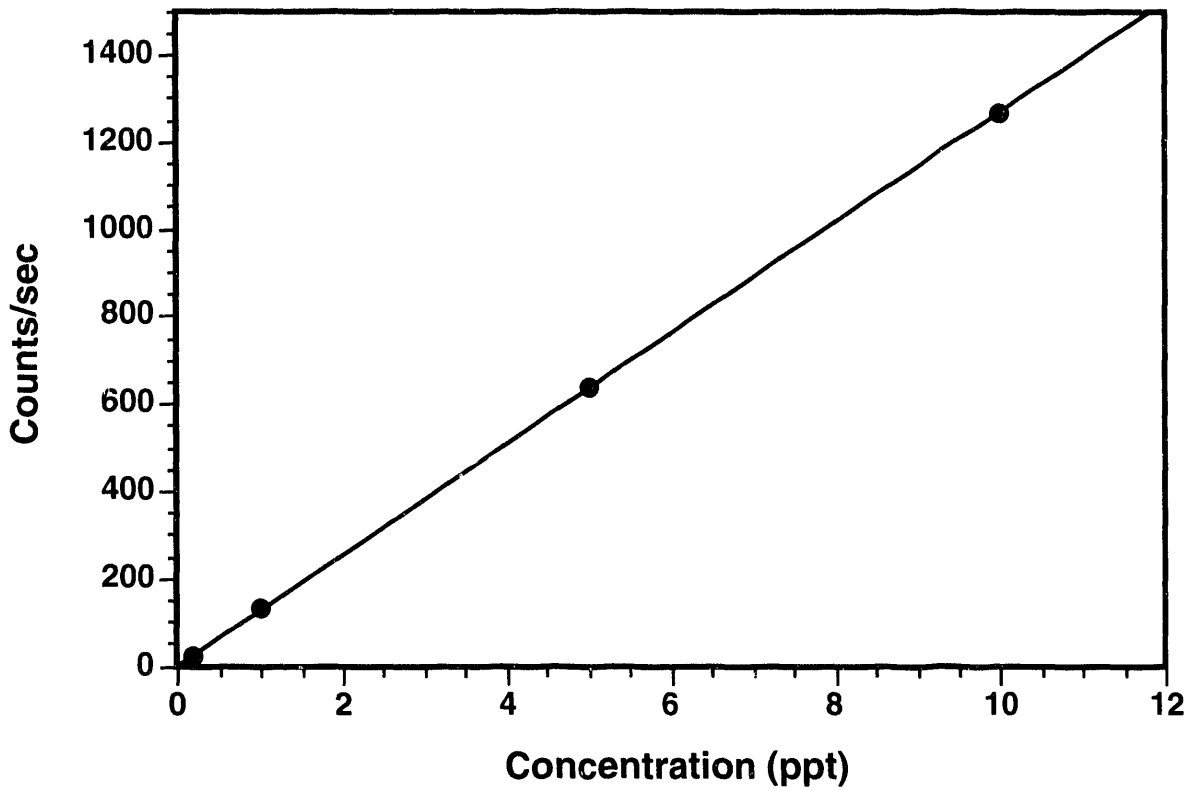


Figure 5. Pu-239 Calibration Curve. One mL standards analyzed using USN and peak-hopping. One measurement one taken for each data point, therefore error bars are not included.

Substantial improvements may also be possible in sample introduction efficiency. A sample transport efficiency of >50% should be attainable, and would probably result in an additional 2 to 5X improvement in instrument response. Ongoing research in ion "trapping", in which ions of a given mass are collected over time and subsequently released for detection, may also have applications in improving ICP/MS detection limits.[3]

The ICP/MS background count rate of 10 to 50 counts/sec greatly limits the technique's ultimate detectability. Although some of the parameters that contribute to the background remain a mystery, recent modifications to an ICP/MS in our lab that involved the isolation of the torch box resulted in reducing the background count rate to approximately one count/sec. Reducing the electronic, radiofrequency, and photon "noise" through additional improvements in design should result in further decreasing the overall background count rate.

CONCLUSIONS

ICP/MS is a viable alternative to alpha spectrometry for measuring ^{239}Pu in urine. Following the described separation procedure using USN as the method of sample introduction and peak hopping as the method of data acquisition, the resulting ICP/MS detection limit for ^{239}Pu in urine (~50 fg) is comparable to that by alpha counting, and can be obtained in seconds rather than days (not including preparation time). The advantage of using ICP/MS over decay analysis becomes more apparent for radionuclides that have longer half-lives, because far more atoms are present than is activity.

Because it is a relatively new analytical technique, the full potential of ICP/MS has not yet been realized. Current research in improving instrument design and sample introduction should result in extending current detection capabilities, which will undoubtedly further promote its extensive use in radiological applications.

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References

1. Smith, M.R., Wyse, F J., and Koppenaal, D.W. *Radionuclide Detection by Inductively Coupled Plasma Mass Spectrometry: A Comparison of Atomic and Radiation Detection Methods.* Journal of Radioanalytical and Nuclear Chemistry, Articles, Vol. 160, No. 2 (1992) 341-354.

2. Wyse, E.J. *Inductively Coupled Plasma Mass Spectrometry (ICP/MS) as an Alternative Method for Measuring Long-Lived Radionuclides in Environmental Material.* Masters Thesis. University of Washington, Seattle, Washington. April, 1991.

3. Koppenaal, D.W., Barinaga, C.J., and Smith, M.R. *ICP/MS Back to the Future with Ion Trap Mass Spectrometry.* 1992 Winter Conference on Plasma Spectrochemistry; San Diego, California; January 6-11, 1992.

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