Application of Non-radiometric Methods to the Determination of Plutonium

LITERATURE REVIEW CONDUCTED FOR
THE BURIED WASTE INTEGRATED PROGRAM

MARCH 5, 1992

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Prepared for the U.S. Department of Energy
Office of Environmental Restoration and Waste Management
Office of Technology Development
Buried Waste Integrated Demonstration Coordinator and Staff
under Contract W-7405-eng-82

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Printed in the United States of America

Available from
National Technical Information Service
U.S. Department of Commerce
5265 Port Royal Road
Springfield, VA 22161

IS-5085

UC-2

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Introduction

This report was motivated by discussions that took place during a review of contamination control technologies proposed for application at INEL. After a presentation by Guy Loomis (INEL) that discussed the planned use of novel counting instrumentation to monitor Pu liberated during remediation activities, George Newton (ITRI) asked whether ICP-MS could be used to make the required measurements. [It is important to make such measurements to determine when contamination control systems must be activated.] Loomis said that he was interested in learning more about the capabilities of ICP-MS for trace actinide measurements. Later in the same session, another speaker described ICP-MS work at LANL aimed at monitoring Pu in air borne particulates. Finally, Martin Edelson (Ames) mentioned that several DOE laboratories were currently evaluating and, in some cases, using ICP-MS for actinide measurements; he also noted that ICP-MS can measure hazardous materials (e.g., Pb, As, Hg, etc.) that could be liberated during remediation activities and that the counting methods would not be able to monitor such materials. In the proposal evaluation conducted on the following day, the review panel discussed the potential for ICP-MS and other non-radiometric methods of analysis for "real-time" Pu analysis and concluded that there was sufficient interest to recommend that the capital funding requested for radiometric equipment be put on hold pending the completion of this review of non-radiometric methods of Pu analysis.

In a letter, dated 1/28/92 from K.M. Kostelnik, Program Manager of BWID, the attention of this report was directed to three specific areas. Kostelnik stated,

Assuming DOE concurrence, this letter transmits the Contamination Control Projects needs for the Ames Laboratory literature search. The literature search should be a valuable tool in identifying non-radiation measurement techniques for plutonium and americium such as ICP-Mass Spec. The following requirements for that study will help compare the ICP type techniques with the radiation measurement techniques such as the large area detector and U-L-shell X-rays:

1. The apparatus must be field deployable and capable of fitting in a trailer towable by a tractor-trailer.
2. The type and proficiency level of operations staff must be clearly defined. For a successful operation, up to 100 samples per day will be required which is more suitable to technician work.
3. The operation must list the lower levels of detection in terms of the amount of plutonium per gram of sample and the time required for the entire process must be carefully accounted for. As an example, if there is extensive chemistry involved in preparing samples, this time must be included in the overall evaluation time. Samples will include up to 10-g soil samples, filters, and smears.

Radiometric and non-radiometric properties of Pu

Plutonium is radioactive and is most usually measured analytically by methods that detect products of its radioactive decay. Several isotopic forms of plutonium exist as a result of nuclear fuel cycle activities; each isotope has a characteristic half-life that determines its "specific activity" (i.e., the number of decay events per gram of the pure isotope) and decays by a specific pathway. Thus Pu-242 decay is accompanied by the production of an alpha particle that can be monitored but Pu-241 decay does not produce an alpha particle and must be monitored by gamma ray or beta particle detection. The commonly encountered isotopic forms of Pu (the 238, 239, 240, 241, and 242 isotopes) have half-lives that range from 14.0 y to 379,000 y [Table 1] and therefore have vastly different specific activities. This suggests that the isotopes can have markedly different hazards to human health and the environment.

Since most Pu detection is accomplished using a decay monitoring technique and the audience of this report is expected to be familiar with these methods they will not be described here in detail. However, when appropriate, current radiometric methods will be compared to non-radiometric methods for Pu determination.

Non-radiometric methods of analysis can be subdivided into those with isotopic selectivity and those with elemental selectivity. It would seem, given the previous discussion, that methods lacking isotopic selectivity could be dismissed immediately from further consideration since they cannot distinguish between the isotopic forms of Pu. This may not actually be the case when there is sufficient prior information regarding the isotopic composition to permit a reasonable conversion of measured Pu concentration into sample activity using known specific activities. Another consideration is the use that the measurement will serve ... if the Pu measurement is for "screening" purposes or is needed to determine whether a threshold value has been exceeded, a rapid elemental determination may be preferable to a more time-consuming isotopic analysis. In fact, a dual measurement strategy that utilizes elemental detection for threshold measurements and triggers an isotopic measurement when the threshold is exceeded might provide the best combination of speed and accuracy for many measurement situations.

Non-radiometric methods

Optical spectroscopic methods

Optical spectroscopy has been used to monitor the concentration of materials since the time of Bunsen. Emission spectrometry relies on the "fact" that when energy is absorbed by an atom or ion, it will quickly relax to its electronic ground state by emitting a photon at a wavelength characteristic of the excited atom. Over 100 years ago, Bunsen and Kirchhoff were able to identify cesium as an element by showing that its emission spectrum was unlike that of any other element previously isolated [1].

Analytical optical emission spectroscopy was revolutionized in the past 20 years with the introduction of laser-based methods for sample ablation and high-resolution spectroscopy and the inductively coupled plasma (ICP) for the inorganic analysis of solutions. The ICP provides an unusually efficient and convenient way to convert a liquid sample into a highly ionized, atmospheric pressure plasma. The plasma emits light that can be analyzed by a monochromator to determine the intensity vs. wavelength spectrum, which is often quite complex. The analysis of this spectrum provides information about the solution components. This procedure is the basis of ICP-atomic emission spectrometry (ICP-AES). ICPs are routinely available from a variety of commercial sources throughout the world and now feature small solid-state power supplies, generally rated to produce ~1.5 KW at 40 MHz. Commercial vendors have also prepared ICP sources that operate directly with air (generally plasma formation is initiated with argon) and with a variety of other gases such as He and N₂, however the ICP is usually operated using Ar.

Mass-spectrometry

Mass spectrometry is a sensitive instrumental method that determines the composition of materials by analyzing the mass-to-charge ratio of their ions. It is important to note that mass spectrometry is not an element-specific detection method and cannot distinguish between isobars (i.e., different elements with the "same" atomic mass such as Pu- and U-238) unless ultra-high resolution instruments, found in only a few research laboratories in the world, are utilized. A large variety of ionization schemes can be employed to convert a sample to an ionic form that can be mass analyzed. Thermal ionization mass spectroscopy is routinely used to determine Pu for nuclear safeguards material accountancy [2] and is capable of great accuracy, precision, and sensitivity. Separative chemistry is required to remove U and other potential interferents (e.g., Am-241) prior to the mass spectrometric analysis of Pu although selective adsorption by chemically-coated resin-beads followed by thermal ionization at temperatures chosen to preferentially liberate selected actinides can be used to eliminate the chemical pretreatment step [3].

ICP-Atomic Emission Spectrometry

When aerosols, generally formed from dilute solutions by devices called "nebulizers," are injected into an ICP source, the intense source heat decomposes the small particulates into constituent atoms with very high efficiency. These atoms are then ionized through a variety of processes and excited to unstable electronic energy states. The excited ions and any unionized atoms return to their stable electronic states by emitting light; the wavelengths emitted are characteristic of the elements in the plasma and can be used to determine their relative concentrations in the original aerosol (and the original solution sample). The determination of sample composition through the measurement of emitted light intensity from an ICP source at characteristic elemental wavelengths is referred to as ICP-atomic emission spectrometry (ICP-AES).

ICP-AES is routinely used in nuclear facilities throughout the world for the determination of trace impurities in a variety of materials including U and Pu [4,5]. Various groups have investigated the use of ICP-AES for the determination of the actinides themselves and have established that such determinations can be made with great sensitivity. For example Huff and Bowers at the Argonne National Laboratory [6] have reported ICP-AES detection limits for Np (39 $\mu\text{g/L}$), U (68 $\mu\text{g/L}$), Cm (2.9 $\mu\text{g/L}$), Pu (28 $\mu\text{g/L}$), and Am (1.9 $\mu\text{g/L}$). Even though the ICP-AES spectrum is often quite complex with a single element emitting light at many discrete wavelengths, Claudon et al [7] were able to simultaneously determine Am and Pu in the presence of U at ratios of U/Pu and U/Am up to 100. Ordinarily ICP-AES instrumentation cannot resolve signals from individual isotopic wavelengths although where the isotope splitting is very large even standard instrumentation can achieve isotopic resolution. This is the case with U and the 235-238 splitting has been resolved with ordinary commercial instrumentation [8]; the 239-240 isotopic splitting of Pu emission lines is ordinarily at least a factor of three smaller than the 235-238 splitting of U lines and cannot be resolved with "ordinary" commercial ICP-AES instrumentation (see "High-resolution ICP methods" below for further details).

Innovative methods have recently been applied to the formation of the aerosol fed into the ICP. Ultrasonic nebulization [9] has been used to improve the efficiency of the solution-to-aerosol conversion process and has resulted in improved ICP-AES detection limits. A great deal of attention has been devoted to methods of direct solids sampling [10,11] to eliminate the need for the preparation of solutions from solid samples. Laser ablation has been used to directly convert solid materials (e.g., metals, glasses [12], and soils [13]) into particulates for introduction into ICP sources. Pang et al [11] determined that a high-repetition rate excimer laser (100 Hz at 308 nm) could be used to convert a solid into a particulate by ablation and determined components of steel (Fe, Ti, Cu, and V) in the solid by both ICP-AES (12 $\mu\text{g/g}$ detection limit) and ICP-MS (4 ng/g detection limit). D'Silva et al [13] have demonstrated that U in soils can be directly sampled via laser ablation using a Nd-YAG laser transmitted through many meters of optical fiber and the resultant particulate transported via hollow tubing into an ICP-AES instrument for analysis. U detection by this method (detection limit < 1 $\mu\text{g/g}$) will be demonstrated at the Fernald site in September 1992.

The precision and accuracy of ICP methods is often improved by removing the elements of interest (the "analytes") from uninteresting majority species (the "matrix") prior to ICP-AES (and MS) analysis. Methods to dissolve refractory materials (e.g., soils and glasses) and to separate the matrix from the analytically-interesting species have undergone recent improvement through the introduction of microwave dissolution methods [14] and new column chromatographic materials [15]; high-pressure chromatography has been demonstrated to reduce the time needed for column separations [16]. These methods of sample preparation are in use in many laboratories throughout the DOE complex on a daily basis and there are commercial ICP-AES instruments currently manufactured for operation in mobile laboratories [17]. ICP-AES work is routinely performed by technicians and commercial instrumentation exists to automate many of the tedious steps and improve sample throughput. With microwave dissolution and chromatographic column separation, it should be possible to dissolve, separate, and analyze over 100 samples of siliceous samples such as soil per 24-hour day by ICP-AES. This instrumentation will capably determine the actinides in soils at the detection limits cited previously; it should be possible to "spike" standard soils with certified reference solutions of Pu of known isotopic composition and carry them through the entire analysis to determine recovery factors, method accuracy and precision, and detection limits. However it must be noted that conventional ICP-AES instrumentation will not be capable of resolving individual actinide isotope emission lines and therefore supplementary information about isotopic composition will be required to transform elemental concentrations into activity levels for comparison with regulatory guidelines.

The application of laser ablation to ICP-AES eliminates the need for time-consuming and labor intensive sample dissolution and chemical separation procedures. It will, however, be necessary to raster the laser across samples to obtain statistically-valid representations of sample composition and it may be necessary to pretreat the sample by careful grinding and sieving to prevent errors from Pu "hot particles" (i.e., in [18] it was noted that Pu could occur as discrete, hot particles, which "tend to withstand ball-milling or normal soil particle size reduction techniques," in a relatively low radioactivity matrix at the Nevada Test Site) from biasing the analysis. It should be possible to analyze over 100 samples per 24-hour day and, if the instrumentation cited in Ref. 13 is successfully demonstrated in the field, the method will be proven "field-deployable." The detection limit for Pu determination by this method is not yet established but should be comparable to the previously cited range of 1 - 12 $\mu\text{g/g}$ for U analysis. It should be noted that primary analytical standards for this method may be difficult to obtain and there is little precedence for regulatory acceptance for ICP-AES analysis using laser ablation for sample introduction whereas conventional ICP-AES methodology for the determination of Pu has great similarity to methods already approved by the USEPA. We also note that glove box housed ICPs are now commercially available and there is a body of experience about operating such devices [19].

High-resolution ICP-AES

High-resolution ICP-AES was pioneered in the US by the Nuclear Safeguards group at the Ames Laboratory. It was developed to test the feasibility of using ICP-AES to perform multi-elemental and multi-isotopic determinations of U and Pu in very radioactive nuclear fuel cycle process solutions. The technique of high-resolution ICP-AES and the successful demonstration of U and Pu isotopic assay was recently reviewed by Edelson [20]. The most notable benefit from the application of high-resolution techniques to ICP-AES is the improved ability to perform isotopic determinations. This is not true universally but applies particularly to actinide elements whose high atomic weight reduces the Doppler widths of spectral lines and whose electronic transitions have large isotopic splittings. U and Pu isotopic analyses have been successfully performed on fuel dissolver solutions in a test of the Ames Laboratory high-resolution ICP-AES technology [21]. It was possible to determine U isotope ratios and elemental Pu concentration in these solutions without the need to separate U from Pu. Due to the low concentration of Pu in the concentrated U matrix and the high Pu-239/Pu-240 isotope ratio in the solution, it was necessary to perform a simple ion exchange separation of Pu from U prior to the Pu isotopic analysis. Generally, the accuracy of these measurements was acceptable, but the precision was much poorer than achieved with isotope dilution mass spectrometry on the same solutions. Other notable features of high-resolution ICP-AES are the elimination of certain spectral interferences and the general improvement of detection sensitivities. It should also be noted that even using a high-resolution monochromator, the ICP-AES detection limits are quite a bit poorer than those obtained with ICP-MS.

Vendors manufacture high-resolution ICP-AES instrumentation that, in principal, should be capable of combining some of the best features of ICP-AES (e.g., elemental specificity, rapid analysis, freedom from isobaric interferences, complete isolation of the instrumentation from radioactive materials) with those of ICP-MS (e.g., isotopic selectivity, improved accuracy through isotope dilution spectrometry). A potential drawback of this approach is the need to provide a well-conditioned environment for the high-resolution spectrometer to preserve wavelength stability. One vendor, Sopra, offers a high-resolution monochromator in a temperature-stabilized enclosure that reduces the need for environmental controls in the spectroscopic laboratory. [Note that the test of high-resolution ICP-AES in Ref. 21 was done in a room with metal walls and floors in a room with poor temperature control. The temperature of the monochromator was not actively stabilized but the monochromator was placed within a Plexiglas enclosure to reduce the influence of drafts and to prevent any transfer of contamination to the monochromator.]

ICP-Mass Spectrometry

The discussion of mass spectrometry for Pu analysis in this report will focus on the technique of ICP-mass spectrometry (ICP-MS) in which sample ionization is accomplished within an ICP source and ions are extracted from the plasma for mass analysis [22]. The chief advantages of using an ICP to produce ions for mass spectrometry are:

1. The ICP operates at atmospheric pressure and samples can be rapidly changed without the need to break and then reestablish vacuum conditions.
2. The ICP source efficiently produces singly charged ions in an inert gas mixture. Oxide formation is very inefficient.
3. The ICP is an intensely hot source (i.e., ~6000 - 10000 K) that efficiently atomizes and ionizes even very refractory elements. The ionization of one analyte is not significantly affected by the presence of other analytes or matrix components. When such effects are noted they can be corrected via internal standardization.

The application of ICP-MS to nuclear industry measurement problems was discussed as early as 1986 [23]. The advantages of ICP-MS over ICP-AES were cited as:

1. ICP-MS has detection limits that are often a factor of 1000 better than achieved with ICP-AES.
2. ICP-MS can perform isotopic analyses that cannot be generally performed via ICP-AES; ICP-MS can utilize isotope dilution methods to enhance analysis precision.
3. The ICP-MS spectrum of actinides is considerably simpler than the ICP-AES spectrum and hence is easier to analyze. Whereas the ICP-MS spectrum of pure U would have fewer than ten peaks due to U (i.e., from the three natural isotopes, the doubly charged ions of those isotopes (very minor peaks), and the oxides of the isotopes (again, very minor peaks), the ICP-AES spectrum would have thousands of emission lines due to the U ion [24].

Several recent papers have compared ICP-MS analyses of actinides against more conventional analytical methods. Kim et al. [25] determined Pu-240/Pu-239 ratios in environmental soil samples via ICP-MS and compared their results against those obtained by the fission track method. The authors found that the ICP-MS method was simpler than the fission track method and, with the addition of a Pu-242 standard, could quantitate the individual isotopic concentrations. Note that the samples tested contained Pu at ultra-trace levels (e.g., ~10 Bq/kg of soil). The same group compared ICP-MS against neutron activation analysis for the determination of environmental levels of Np-237 in soils [26]. ICP-MS was found to have higher precision, accuracy, and better detection limits than NAA. Hall et al [27] discussed the use of electrothermal

vaporization to improve detection limits in ICP-MS so that femtogram quantities of U and Pu could be determined (this hyphenated technique, called ETV-ICP-MS, requires μL samples). Were this sensitivity obtainable, it would be possible to utilize ICP-MS for the analysis of Pu and U in urine and replace α -spectroscopy for worker dose monitoring. The authors successfully demonstrated detection of Pu-244 at the 10^6 atom limit using a single-ion monitoring mode; detection at the 10^7 atom level was demonstrated in multi-ion mode for the determination of Pu-242/Pu-244 mixtures. The authors noted that ICP-MS could not measure Pu-238 at levels necessary for worker monitoring (sub-femtogram) due to inadequate detection limits and the impossibility of obtaining reagents and materials that do not contain sub-trace levels of U-238 that could interfere with Pu-238 measurements.

Isobaric interferences do not preclude the determination of U in urine for health physics monitoring where it is necessary to quantitate U-234 with very great sensitivity (16 ppt detection for U-234 is mandated by an ANSI standard [28]). Stewart at ORNL is currently developing an ETV-ICP-MS method for U isotopic analysis that uses column chromatography to separate U from the complex electrolytic matrix found in urine. Laboratory experiments have demonstrated that the required sensitivity is attainable; the method is now being written and QA/QC data obtained to support the laboratory results [28]. Gladney et al at LANL [29] compared the use of conventional ICP-MS versus delayed neutron assay (DNA) for monitoring U-235 in worker urine. The "concern level" for enriched U at LANL is 30 pCi/L; the "concern level" for depleted U is 30 $\mu\text{g/L}$. ICP-MS detected U-235 at these levels without the need to remove the matrix or concentrate the solution by evaporation. Gladney et al stated, "The use of ICP-MS for the determination of U in urine is fast, accurate, requires little sample preparation and provides direct isotopic information. It compares well with DNA as a screening method in overall cost and provides comparable or better sensitivity."

Stewart has investigated the use of ETV-ICP-MS to determine transuranic elements trapped in large air filters. Pu, Np, and Am were determined at 5 fg levels after ashing the filter, leaching the ashes in hot nitric acid, and separating the transuranics from filter materials by column chromatography [28]. An ICP-MS vendor (VG Instruments) has reported the use of laser ablation ICP-MS (LA-ICP-MS) to analyze atmospheric aerosols. In this study air particulates trapped by Whatman Filter papers were ablated and the resulting aerosol introduced into an ICP-MS for mass analysis. Results were obtained for 61 "elements" in a two-minute scan. No detection limit data were presented [30 (included in the Appendix for easy reference)].

ICP-MS, being the product of two mature technologies, has itself rapidly matured. Commercial instrumentation is available from a number of vendors and each has an active applications laboratory that effectively improves the state-of-the-art. The author does not know of any commercial instrumentation that is manufactured for field use but does not see any insurmountable problem with placing an instrument into the field. Since the sample preparation work is almost identical to that required for ICP-AES it should be possible to analyze over 100 samples per 24-hour day and the work should be performable by technician-level staff [28].

Two questions that were not put forward in the ICP-AES section must be answered with respect to ICP-MS. First, since ICP-MS operates at such great sensitivity, it is necessary to determine the laboratory cleanliness required to avoid serious sample contamination and question whether it can be maintained in a field installation. Stewart operates his ICP-MS within a "semi clean-room." All room air is triple HEPA filtered, the room has an air-lock entry, and the room surfaces are painted with epoxy paints that can be easily cleaned. Personnel don "booties" upon entering the room to avoid carrying contaminants into the laboratory. Stewart stated that one reason for the extreme care exercised was that his ICP-MS instrument was used for a variety of environmental measurements -- perhaps U one day and Hg the next -- and that the utmost cleanliness needed to be maintained to avoid sample contamination from almost any source. He suggested that a dedicated instrument, particularly one dedicated to Pu analysis, might not need such stringent isolation. Monty Smith (PNL), who has measured trace levels of actinides via ICP-MS, was queried about the need for instrument isolation. He replied that it was not a substantial problem.

Second, since the sample enters the mass spectrometer for measurement and is either trapped there or is pumped out of the spectrometer, do the spectrometer or vacuum pump become contaminated after routine use and is it difficult to remove built-up contamination? Also, since the samples may exhibit relatively high levels of alpha activity, can the ICP-MS be operated within a glove box enclosure? H. Weismann (Spectrotec GmbH) discussed those questions in the abstract of a presentation at the 1992 Winter Plasma Conference in San Diego jointly authored by him and two workers at the Institut für Transurane (Karlsruhe) [31 (included for easy reference in the Appendix)]. The response indicates that, in this installation at least, neither the mass spectrometer nor the pump was extensively contaminated. Note that no information was provided about the contamination levels of the samples analyzed with this instrument or its frequency of use. A glove box enclosed ICP-MS is now in use at LANL for the analysis of radioactive solutions. Crain [32] reported that LANL has a current proposal under consideration by Rocky Flats for the development of ICP-MS to determine Pu in airborne particulates. He also reported that solutions with high concentrations (~1000 ppm) of Pu seemed to cause excessive wear on the ICP-MS sampling and skimmer cones.

High-resolution ICP-MS

Conventional ICP-MS instruments are provided with quadrupole mass analyzers of limited resolving power ($M/DM < 500$) and mass interferences between certain molecular species and atoms cannot be resolved. This is not too much of a problem at the actinide masses, but serious interferences occur at low masses. Thus, ArO interferes with Fe-56, Ar₂ interferes with Se-80, O₂ interferes with S-32, etc. A high-resolution ICP-MS instrument is commercially available that utilizes a double-focusing magnetic sector mass analyzer to achieve a resolving power adjustable from 3500 to 10000 that can eliminate the aforementioned isobaric interferences [33]. Unfortunately, the increased resolving power is insufficient to resolve atomic isobaric interferences such as those between isotopes of Pu, U, and Am.

The geometry of the high-resolution ICP-MS instrument (the VG Plasma Trace) eliminates one of the noise sources that plague low-resolution ICP-MS instruments, spurious signal from vacuum ultraviolet photons that strike the detector, by presenting the ions with a tortuous path through the mass analyzer that effectively blocks photons from striking the detector. Since no on-axis "photon stop" is required with this device, a relatively larger fraction of ions is collected (resulting in a greater signal) than can be collected with a low-resolution ICP-MS. These advantages translate into better detection limits. Whereas the detection limit of U generated by laser ablation using a conventional ICP-MS is ~2 ppb, it is improved to ~28 ppt with the high-resolution ICP-MS instrument; with a standard nebulizer the detection limit for U determination is improved from 200 fg/ml to <50 fg/ml [34].

ICP-Atomic Fluorescence and Laser Excited Atomic Fluorescence Spectrometry

Once atoms and ions are formed from a sample by an ICP they can be analyzed by a number of spectroscopic methods. ICP-Atomic Fluorescence and Laser Excited Atomic Fluorescence Spectrometry are techniques that utilize supplementary optical sources, hollow cathode lamps and lasers respectively, to selectively promote plasma species to excited electronic states and then monitor the light emitted (fluorescence) when they return to a lower energy state. In principal, this form of ICP optical spectroscopy is more selective than optical emission spectroscopy since both the optical source wavelength and the fluorescence wavelength can be selected to be characteristic of the analyte under investigation.

The original work in ICP-AFS was reported in 1976 [35] and spawned a commercial product manufactured by the Baird Corporation (AFS-2000). Later work in many groups centered upon the application of tunable lasers to generate fluorescence in plasmas. Human et al [36] reported a 20 $\mu\text{g/L}$ detection limit for U detection by ICP-LEAFS, which is better than Huff's ICP-AES detection limit (68 $\mu\text{g/L}$ [6]). Berthoud et al [37] reported a 50 $\mu\text{g/L}$ detection limit for the determination of Pu by ICP-LEAFS and postulated that, after experimental refinements, the ultimate detection limit would be closer to 1 $\mu\text{g/L}$. This paper contained the important result that ICP-LEAFS, because of its inherent selectivity, could determine Pu in concentrated U matrices (30 000:1 ratio of U to Pu) without the need for chemical separations. Such a determination could not be done by ICP-AES, even with high resolution detection.

ICP-LEAFS is thus characterized as a very selective and sensitive detection method. It suffers from the added complexity imposed by the need to have a tunable laser for fluorescence excitation. It is best characterized as a single-element technique whereas ICP-AES and ICP-MS are true multi-element analysis techniques. For very specialized measurements ICP-LEAFS can offer advantages relative to the other ICP methods. It does not suffer isobaric interferences, such as trouble ICP-MS, and can easily resolve Pu from U or Am; with greater selectivity than ICP-AES, it has negligible spectral interferences and could eliminate the necessity for many chemical separations. The sensitivity of ICP-LEAFS lies between the two other ICP methods. To the best of the author's knowledge there are no commercial suppliers of ICP-LEAFS instrumentation but laboratories can generally construct instruments from commercially-available subsystems.

High-resolution ICP-LEAFS

High-resolution ICP-LEAFS (HR-ICP-LEAFS) is accomplished by using a narrow-line dye laser for fluorescence excitation. Vera et al [38] recently demonstrated that HR-ICP-LEAFS was capable of isotopic discrimination by resolving the 235-238 splitting of selected U ion spectral lines. The detection limit reported in that reference for U has been lowered from 2000 $\mu\text{g/L}$ to ~500 $\mu\text{g/L}$ by replacing the nebulizer previously used with an ultrasonic nebulizer [39]. This improved sensitivity was still poorer than was achieved by Human et

al [19] (500 $\mu\text{g/L}$ vs 20 $\mu\text{g/L}$ detection limit). However, it really isn't fair to compare these numbers since the U lines in Ref. 38 were chosen for their large isotopic splitting and not for their intrinsic line strength.

As in all high-resolution spectrometry, one achieves improved selectivity and sensitivity at the expense of additional instrumental complexity. It is likely that current HR-ICP-LEAFS instrumentation could not be operated successfully by technicians since the lasers often require realignment. The successful adaptation of ICP-LEAFS to the non-research laboratory requires that the laser portion of the apparatus be simplified and made less costly. To that end it is interesting to note that diode lasers have recently been shown capable of actinide detection [40]. Should such lasers be usable with the ICP source for LEAFS, this technique could be very competitive with other ICP spectrometries.

Resonance Ionization Mass Spectrometry

Resonance ionization mass spectroscopy (RIMS) is a technique capable of great selectivity and sensitivity and has been successfully applied to the determination of Pu [41 - 44]. This method, as applied in the past [44], involved depositing the Pu sample electrolytically upon a Re filament that was subsequently overcoated with a Re layer to "... obtain a slow evaporation in a neutral, non-molecular form at filament temperatures of about 1800 K." The Pu liberated by evaporation was then irradiated with a laser tuned to a Pu absorption line and driven to ionization by the absorption of a second photon from the same source or photons from additional lasers. The resulting ions were mass analyzed to complete the isotopic determination. The elemental selectivity in the laser ionization step can be as great as 10^9 and the mass analyzers used (both time-of-flight, with a resolving power of ~ 700 , and double-focusing sector instruments have been used) can easily achieve unit mass resolution. Thus RIMS should not suffer from the isobaric interferences that occur in ICP-MS. In principal, RIMS should be capable of almost single-atom detection, but the best sensitivity obtained to-date is $\sim 10^6$ atoms, which is a factor of ten better than that obtained via ETV-ICP-MS in multi-ion mode.

A commercial firm, Atomsciences (Oak Ridge, TN), has been actively developing RIMS for diverse applications for about 10 years. They are currently evaluating a "new" atomization source, a graphite oven, for application in RIMS. This source, used for many years in atomic absorption spectrometry, promises to make the application of RIMS to environmental samples feasible. The RIMS apparatus has a small "footprint" and could be operated in a mobile laboratory. According to the President of Atomsciences [45], the laser analysis only requires ~ 5 minutes/sample and new samples can be loaded into the instrument and the pressure reduced to operating pressures in as little as 10 minutes; best results are obtained if the matrix is separated from the analyte prior to RIMS analysis. Laser ablation has been used to atomize materials prior to selective laser irradiation but analytical quantitation was reported to be difficult [45].

Discussion

The selection of an analytical technique for the monitoring of Pu for contamination control at BWID requires the judicious evaluation of several factors:

1. Will Pu isotopic information be required?
2. How quickly must a measurement be made and the results available?
3. How sensitively, accurately, and precisely must Pu be measured?
4. Is Pu the only material that needs to be monitored? If not, would it be useful to have multielemental analysis capability in the instrument used for Pu measurements?
5. Will the matrix that contains the Pu be consistent from measurement to measurement?

Murray [46] prepared a summary of analytical techniques for Pu determination that included a survey of many nondestructive and destructive methods. Information from that survey relevant to the questions listed above is summarized in Table 2. It is clear that many candidate non-radiometric methods for Pu analysis were not discussed explicitly in this report.

The sensitivity of the ICP methods and RIMS can be compared against the sensitivity needed for contamination monitoring at INEL. This sensitivity, given in radiometric terms as $2 \times 10^{-8} \mu\text{Ci/cc}$ [47], is converted into absolute masses for selected radionuclides in Table 3. Table 3 also contains calculated values for the expected solution concentration of individual radionuclides collected by a filter (25 cfm) in one hour and reduced to a matrix-free solution by ion exchange chromatography. It is assumed that the pretreatment would result in a loss of 50% of the analyte with the remainder dissolved in a 10 ml solution (recall that this loss can be determined by isotope dilution measurements). Only Pu-241, a β -emitter, with a required detection limit of 400 ppt, would challenge the sensitivity of ICP-MS. Pu-238, requiring better than 2 ppb detection, would be easily determined. In fact, assuming that Pu-238 could be determined in solution at 30 ppt and that Pu-241 would not need to be monitored, it should be possible to determine whether safety limits have been exceeded by collecting air particulate samples at 25 cfm for only 1 minute. Of course the analysis would take much longer than one minute because the dissolution of the sample and the chemical separation needed to isolate Pu-238 from U-238 requires substantially longer than 1 minute to accomplish. The need to determine Pu-238 and Am-241 in the presence of U-238 and Pu-241 seems to preclude the possibility of using laser ablation ICP-MS for Pu monitoring.

There is little evidence to suggest that ICP-AES and -LEAFS methods have sufficient sensitivity to determine Pu-238 at the 2 ppb level with confidence but RIMS should have sufficient sensitivity. Since RIMS involves selective excitation prior to ionization, and subsequent mass detection, it is possible that U-238 and Pu-241 would not need to be chemically separated from Pu-238 and Am-241 prior to the RIMS analysis. According to Thonnard [45], the selectivity of resonance ionization can be as great as 10^9 , which should exceed the concentration ratios of U-238/Pu-238 and Pu-241/Am-241 in the sample (according to Stewart [28] dilute U forms a refractory carbide when heated in a

graphite tube, which should effectively strip the U from sample solutions and reduce the U/Pu ratio). However, the efficiency of atomization using a graphite oven and the efficiency of signal ion collection in the mass spectrometer will be deleteriously affected by very concentrated matrix components. Thus RIMS detection limits for Pu could deteriorate if the instrument were confronted with the task of determining Pu in a complex matrix.

Since ICP-MS and RIMS are so very sensitive, it is reasonable to ask again whether they can be accomplished in field-deployable, mobile laboratories. Both Stewart and Thonnard declared that, given sufficient care, such installations should be feasible and ICP-MS is effectively used for ultratrace analysis in many laboratories throughout the world. Clearly, great care will need to be exercised to prevent U contamination of the laboratory air, reagent solutions, and the ICP-MS instrument.

Most of the time required for the ICP-MS determination of Pu will be taken by the sample dissolution and the separation of U from Pu. Real gains in sample throughput and total analysis time would result from optimization of these steps.

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Tables

Table 1. Radiological Properties of Selected Isotopes*

Element	Isotope	Half-life	Primary decay mode	Specific Activity (Ci/g)**	Notes
Radon	222	3.824 d	a 5.486 Mev	1.16	
Radium	226	1600 y	a 4.781 Mev	0.99	
Thorium	232	1.41E10 y	a 4.01 Mev	1.09E-07	100% nat. abundance
Uranium	234	2.47E5 y	a 4.77 Mev	0.006	0.0057% nat. abundance
	235	7.1E8 y	a 4.396 Mev	2.15E-06	0.72% nat. abundance
	236	2.39E7 y	a 4.49 Mev	6.35E-05	
	238	4.51E9 y	a 4.20 Mev	3.34E-07	99.27% nat. abundance
Neptunium	237	2.14E6 y	a 4.79 Mev	0.0007	
Plutonium	238	86 y	a 5.50 Mev	17.5	
	239	2.44E4	a 5.157 Mev	0.061	
	240	6580 y	a 5.17 Mev	0.227	
	241	14.0 y	b 0.021 Mev	106.1	a 4.90 Mev (0.002)
	242	3.79E5	a 4.90 Mev	0.004	
Americium	241	433 y	a5.49 Mev	3.43	

*Taken from, "American Institute of Physics Handbook," 3rd Ed., D.E. Gray, Coord. Ed., Mc-Graw-Hill, New York, NY 1972, pp. 8-79 - 8-87.

**Specific activity (Ci/g) = $0.693 \times 6.02E23 / (GAW \times \text{half-life (s)} \times 3.7E10)$
 $= 1.13E13 / (GAW \times \text{half-life (s)})$ or
 $= 3.58E5 / (GAW \times \text{half-life (y)})$

Table 2. Comparison of Analytical Techniques for Pu Determination
(Adapted from information provided in Ref. 46)

Technique*	IA?	Speed	Sensitivity (gPu/g)	Accuracy	Precision	F D?	Avail- ability
Alpha spectrom.	No	1-2 d.	1 pg	1 pg	1 pg	Y	Comm
Gamma spectrom.	Y	1-2 h.	μg-mg	1-5%	1-10%	Y	Comm
X-ray fluoresc.	No	2-6 h.	50 ng	0.3%	-	Y	Comm
Fission track	Y	1-2 d.	-	10%	6-13%	-	R&D
Neutron irradi.	Y	1-2 d.	μg	3-6%	-	-	R&D
Neutronometric	No	1-2 d.	20 μg	-	10%	-	Comm
Thermal ioniz. MS	Y	1-2 d.	1 ng	Good	0.3%	-	Comm
RIMS	Y	1 h	100 fg	Good	1%	Y	Comm
ICP-MS	Y	1 h	<1000 fg	1-5%	2-5%	Y	Comm
Coulometry	No	1-2 d.	200 pg	1%	0.2%	?	Comm
Titrimetry	No	1-2 h.	1 - 100 mg	0.1%	0.15%	Y	Comm
Polarography	No	8 h	10 - 50 mg	1%	1%	Y	Comm
UV-Vis. Absorp.	No	>6 h	1 μg - mg	5%	1-2%	Y	Comm
ICP-AES	Y	1 - 2 h	15 ng	5%	5%	Y	Comm
ICP-LEAFS	Y	1 - 2 h	50 - 500 ng	10%	10%	-	R&D
Calorimetry	No	1 - 2 d	g - kg	-	0.08%	?	Comm

*Techniques in boldface were discussed in the text. Information for boldface items in Ref. 46 was updated with information gathered for this report.

IA = isotopic assay; FD = field deployable; included in "Speed" is expected chemical pretreatment time.

NB Sensitivity listings can be confusing - in some cases specialized analysis situations are covered (e.g., for polarography, the citation refers to a determination of U/Pu in fuel dissolver solution containing a large amount of U).

Table 3. Target Radioactivity Levels Converted to Solution Concentrations

Element	Isotope	Half-life*	Primary decay mode*	Specific Activity (Ci/g)**	Airborne (μg/cc) [Note 1]	Sample concentration (μg/ml) [Note 2]
Radon	222	3.824 d	a 5.486 Mev	1.16	1.72E-8	0.037
Radium	226	1600 y	a 4.781 Mev	0.99	2.02E-8	0.043
Thorium	232	1.41E10 y	a 4.01 Mev	1.09E-07	0.18	3.8E5
Uranium	234	2.47E5 y	a 4.77 Mev	0.006	3.33E-6	7.07
	235	7.1E8 y	a 4.396 Mev	2.15E-06	9.3E-3	1.98E4
	236	2.39E7 y	a 4.49 Mev	6.35E-05	3.15E-4	6.69E2
	238	4.51E9 y	a 4.20 Mev	3.34E-07	5.99E-2	1.27E5
Neptunium	237	2.14E6 y	a 4.79 Mev	0.0007	2.86E-5	6.07E1
Plutonium	238	86 y	a 5.50 Mev	17.5	1.14E-9	0.002
	239	2.44E4	a 5.157 Mev	0.061	3.28E-7	0.697
	240	6580 y	a 5.17 Mev	0.227	8.81E-8	0.187
	241	14.0 y	b 0.02 Mev	106.1	1.89E-10	0.0004
	242	3.79E5	a 4.90 Mev	0.004	5E-6	10.62
Americium	241	433 y	a 5.49 Mev	3.43	5.83E-9	0.012

*Taken from, "American Institute of Physics Handbook," 3rd Ed., D.E. Gray, Coord. Ed., Mc-Graw-Hill, New York, NY 1972, pp. 8-79 - 8-87.

**Specific activity (Ci/g) = $0.693 \times 6.02E23 / (\text{GAW} \times \text{half-life (s)} \times 3.7E10)$
 $= 1.13E13 / (\text{GAW} \times \text{half-life (s)})$ or
 $= 3.58E5 / (\text{GAW} \times \text{half-life (y)})$

[Note 1]: Concentration equivalent to $2 \times 10E-8$ μCi/cc, which is the INEL limit for entry to contaminated areas by personnel in "bubble suits." (From, G.G. Loomis, D.E. Menkhaus, and D.W. Scott, "A System to Control Contamination During Retrieval of Buried TRU Waste," a presentation at Waste Management 90).

[Note 2]: Concentration of hypothetical analytical sample prepared by dissolution of airborne material. This material, assumed to contain a specified radionuclide at the INEL limit cited in the adjacent column, is contained in 1500 cubic feet (i.e., 1 hour collection at 25 cfm) of air. Chemical purification treatments are presumed to result in the loss of 50% of the sample. The remaining material is dissolved in 10 ml of solution and then analysed.

APPENDICES

**Analysis of Atmospheric Aerosols
using LA ICP-MS**

- ☐ **Rapid, direct determination of airborne particulates**
- ☐ **Full mass range and isotopic information using LA ICP-MS**
- ☐ **LA ICP-MS shows promise for future work in atmospheric studies**

Introduction

Atmospheric studies into pollution of the environment have become of paramount importance. Scientists stationed in the Arctic are studying industrial airborne pollution emanating from the Northern hemisphere. Identification of the origins of these trace metals would enable the movement of airflows around the polar region to be understood more fully. Currently, neutron activation analysis, (NAA), is used to fingerprint airborne particulate deposited on coated cloths. Such analysis is slow, expensive and limited in elemental range. ICP-MS coupled with a laser ablation sample introduction device can be used to analyse airborne particulate collected on filter papers directly. By finger-printing the elemental content of the particulate, conclusions regarding the origin of the aerosol can be deduced. Eastern Europe is thought to be the major contributor of this atmospheric pollution.

Sampling Procedure

A series of samples were taken at various points throughout The Netherlands by drawing ambient air through Whatman Filter papers (5.5 cm diameter). Clean filter papers were also obtained to enable the data to be blank subtracted. In an attempt to quantify a selection of key elements, a range of standard papers was prepared synthetically by drawing known amounts of solutions of each element through a clean filter paper.

Element	Concentration Range
Ca	0 - 100 µg Total
Zn	0 - 50 µg Total
Pb	0 - 20 µg Total

All volumes in this work are expressed as µg Total per paper. Since the amount of air sampled is known, the values could also be expressed per unit volume of air.

A Novel Approach Laser Ablation ICP-MS

The instrumentation used in this study was a VG PlasmaQuad PQ2 TurboPlus, coupled to a VGLaserLab. The system parameters were optimised to achieve sampling of the deposited layer such that the laser event ablated all of the particulate and almost the full thickness of the paper below it.

Analytical Data

Calibration plots for the three elements were obtained. The data was acquired simultaneously in scanning mode and good linearity was achieved at these levels. The calibration plots are shown in figure 1 (see overleaf). Total analysis time per sample was under 2 minutes. The size of the sample analyte distribution had been achieved.

These three elements were quantified in all of the samples:

Concentration Ranges (blank subtracted)

Ca	120 - 2100	µg Total per paper
Zn	40 - 390	µg Total per paper
Pb	120 - 580	µg Total per paper

Reproducibility

3 separate raster sites (1 cm square)

	µg Total		
Sample ES21	Ca	Zn	Pb
	115	134	160
	162	100	96
	100	99	120

The variation is due mostly to the inhomogeneity of the sample. A larger raster pattern would minimise this.

Figure 1 Calibration Curves (units μg Total)

Calcium 42

Zinc 64

Lead 208

Table 1

Single Standard Analysis Results

The Pb value, obtained quantitatively for each sample was entered into the single standard calculation program to give concentration data for all other elements.

Sample HOU 2301			
Be	0.10	Cd	1.2
B	8.2	In	0.04
Na	300	Sn	4.9
Mg	360	Sb	3.3
Al	410	I	2.6
Ca	1500	Te	0.04
Sc	0.23	Cs	0.22
Ti	54	Ba	8.7
V	27	La	0.20
Cr	15	Ce	0.83
Mn	34	Pr	0.09
Fe	440	Nd	0.21
Co	2.0	Sm	0.08
Ni	20	Eu	0.02
Cu	25	Gd	0.02
Zn	410	Tb	<0.01
Ga	1.9	Dy	0.02
Ge	0.78	Ho	<0.01
As	3.8	Er	0.01
Se	0.55	Tm	<0.01
Br	30	Yb	0.01
Rb	2.7	Lu	<0.01
Sr	4.1	W	0.35
Y	0.08	Re	0.01
Zr	0.56	Au	0.01
Nb	0.12	Hg	0.55
Mo	1.1	Tl	0.27
Ru	0.01	Bi	0.27
Rh	<0.01	Th	0.04
Pd	0.05	U	0.10
Ag	1.8		

Conclusions

☐ Neutron Activation Analysis, the technique currently used, is slow, expensive and limited in elemental coverage. Samples must be transported to a reactor and the disposal of irradiated material is a further problem. Elemental fingerprinting is really the only information produced

☐ By comparison, LA ICP-MS is very fast (< 2 minutes per sample), covers the full mass range and generates both qualitative and quantitative data plus the added advantage of isotopic ratios, all from one acquisition

☐ With some further sampling optimisation, this application shows great promise for future work in atmospheric studies

EXPERIENCE OF ICP-MS OPERATION IN THE NUCLEAR FIELD

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Until now there is very little experience available on the operation and maintainance of ICP-Mass-Spectrometers used to analyze radioactive samples.

This poster shows the technical requirements and the maintainance of an Elan-250 ICP-MS with glove box after 3 years of operation in the European Institut of Transuranium-Elements.

ICP-OES instruments with glove box are already a decade or longer in use since ICP instruments came in the market. The fundamental difference in the safety aspect between ICP-OES and ICP-MS is in the separation of glove box and spectrometer.

With an ICP-OES a gas tight connection between spectrometer and glove box is relatively easy with an optical lens or a fibre optic to realize. Service work on the spectrometer itself is therefore routine.

With an ICP-MS there must be during the analysis an opening for the Ion beam. The ions which enter the interface (sampler and skimmer region) do cause contamination. When this ICP-MS with glove box has been installed in 1988 there was no data and information available what type of contamination and in which region of the system it would occur. The poster shows on the photographs the different steps which where taken to open the spectrometer and to change the CEM (Channel Elektron Multiplier).

1.) Argon has been connected to the spectrometer for bleeding the chamber and to pass through a filter paper in an outlet to the vacuum pumps. Filter has been measured with an Alpha, Beta and Gamma counter to see if there is volatile contamination in the system. No measurable intensity has been found on the filter.

2.) With the sliding interface closed the glove box could be separated gas tight from the mass-spec itself.

3.) Gas masks were used when the spectrometer housing has been removed.

4.) Critical sections like the interface outlet, CEM housing, Mass-spec were checked by wiping tests. Most of the contamination then 2-3 cps were found at the interface outlet. No measurable contamination outside the Quadropole and the CEM itself.

5.) By using the correct filters also no contamination has been found on the fore-pumps.

6.) The poster shows that an ICP-MS can be operated safely in the nuclear field.

REMOTE, REAL-TIME ANALYSIS OF HAZARDOUS WASTES THROUGH LASER ABLATION INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

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INTRODUCTION

The Department of Energy has embarked upon an ambitious program to clean up the large number of radioactive and mixed waste sites at the various nuclear energy complexes. Analytical characterization both for inorganics and organics is an essential element of the above task.

An accurate composition of the waste site is essential to the determination of the health and environmental risks posed by that site. Based on the data obtained, remedial strategies can be planned. Field-operable analytical systems that can provide data in real-time have the great advantage that samples especially radioactive need not be collected, catalogued, transported and stored prior to analysis. Also, on-site testing and analysis can provide data to determine that remedial strategies are working. The mobile analytical facility that is being set up at the Ames Laboratory is based on laser ablation and inductively coupled plasma-atomic emission spectrometry (ICP-AES). A robotic sampling system to venture into highly radioactive environments is also being developed.

ANALYTICAL TECHNOLOGY

Inductively Coupled Plasma-Atomic Emission Spectrometry. Currently ICP-AES is utilized worldwide for the characterization of a wide variety of samples for over 70 elements including isotopes (1,2). The technique is also accepted by the Environmental Protection Agency for the characterization of inorganic wastes. The principal components of the instrumentation is the generation of a high temperature plasma (~7000K) in an inert gas such as argon. When a sample, usually a solution is introduced into the central channel of the plasma as an aerosol, the components of the sample are dissociated, atomized and excited to produce characteristic atomic and ionic optical spectra of the atomic constituents of the sample. The atomic spectra are unique signatures of the elements and their isotopes. The spectra are monitored by either a sequential or a simultaneous optical spectrometer. With the latter type of instrument up to 60 elements can be determined in one minute.

Laser Ablation. The conventional approach to analyze solids is to prepare a 1X solution (w/v) of the sample in an appropriate acid mixture. This process is time consuming and is inconvenient for the rapid field analysis of samples. Two alternate approaches for the direct sampling of solids are spark or laser ablation (3). Spark ablation can only be utilized for the direct analysis of solids but not for refractory type samples such as soils. Spark ablation is applicable if soils are incorporated into a conducting solid such as a graphite pellet. In contrast, laser ablation is applicable to the direct

sampling of metals as well as refractories and can be utilized for remote sampling by transmitting the laser radiation through fibers to the desired location. Hence, in our Instrument laser ablation is being utilized for the remote analyses of solids.

Sampling of Liquids. Normally a pneumatic nebulizer (PN) is utilized to introduce an aerosol of the liquid sample into the ICP. The PN is only 1-2% efficient and requires relatively large amounts of samples (~5 mL/min.) The ultrasonic nebulizer (USN) is more efficient (10-30%) and can provide superior limits of detection (LOD) in contrast to the PN but still needs 1 to 3 mL/minute of sample. In contrast to the PN and USN the direct injection nebulizer (DIN) is 100% efficient and can provide analysis on only 100 μ L of sample. Hence, the DIN is preferred for the analysis of radioactive liquids.

Robotic Sampling System. When sampling in a hazardous or highly radioactive environment, it is best to utilize a remotely operated robotic sampling system (RSS). Thus, exposure of personnel to such environments is avoided or minimized. Such a RSS has been designed and a prototype assembled. The design and performance of the RSS will be discussed in a separate presentation.

REMOTE ANALYSIS CONCEPT

The concept for the mobile remote analysis facility can be gauged from Figure 1. A laser beam from a tripled YAG operating at 355 nm is transmitted through a W grade, 600 μ m fiber to a remote location to initiate ablation of a surface or sub-surface sample. The ablated particles, which are generally a few microns in diameter are transferred by a stream of argon (~1 L/minute) to an ICP source positioned on the robotic platform. The optical signal generated in the plasma, which is representative of the sample constituents is transferred through a second optical fiber to a multichannel optical spectrometer situated in the mobile facility to provide data on 20 selected elements simultaneously. Analytical data for the initial studies were obtained from a low resolution 0.5 meter sequential spectrometer equipped with a diode array detector. The time required for the analysis of a single surface sample is generally less than 15 minutes. For the analysis of liquids, the sample is remotely pumped into the DIN.

For obtaining information on the isotopic composition of samples, a high resolution sequential optical spectrometer will be utilized.

DIRECT ANALYSIS OF SOLIDS

One of the major tasks in the remediation program of DOE is the analysis of soils, which contain a wide range of toxic and radioactive elements such as Cr, U and Th. In our initial studies we have been focusing on the determination of U and Th in soils obtained from Fernald. The experimental conditions utilized for LA-ICP-AES studies involving the above type of samples are summarized in Table I.

For the analysis of soils from Fernald, synthetic standards containing U and Th in the range of 10 to 500 ppm were prepared and analyzed utilizing the standard conditions (Table I). The spectrum obtained in 20 sec. from a standard containing 100 ppm of U and Th is shown in Figure 2. This level of U and Th is the remediation level at Fernald. Calibration data obtained by

utilizing Si as an internal reference are shown in Figures 3 and 4. With the current optical spectrometer, the spectral lines of U, Th and Si can be simultaneously imaged on the diode-array detector. The precision and accuracy with matrix matched standards is better than $\pm 10\%$.

The technique can be applied to the analysis of a wide array of samples. The types of samples examined in our initial studies are listed in Table II.

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Table I. Experimental Conditions for Laser Ablation ICPAES

Excimer-Pumped Dye Laser System:

Mode	pulsed
Pulse duration (ns)	10
Wavelength (nm)	400
Repetition rate (Hz)	50
Pulse energy (mJ)	3
Average output power (W)	0.15
Peak power density (MW/cm ²)	100
Fiber optic length (m)	20

Analysis Conditions:

Ablation cell	double-walled glass 20 cm ³ internal volume
Samples	pelleted
Laser spot diameter (mm)	0.5
Raster speed (mm/s)	1
Travel distance (mm)	10
Transport tube length (m)	1
Gas flow rate (L/min)	0.8

Inductively Coupled Plasma:

Rf frequency (MHz)	40
Rf power (kW)	1.1
Reflected power (W)	5
Plasma gas flow rate (L/min)	16
Auxiliary gas flow rate (L/min)	0.2
Sample gas flow rate (L/min)	0.8
Torch	standard

Spectrometer and Detection System:

Focal length (m)	0.5
Grating (G/mm)	2400
Entrance slit width (mm)	0.02
Photo diode array	700 pixel intensified
Signal integration time (s)	10

Table II Samples Analyzed by LA-ICPAES

Uranium Samples	Concentration	Matrix Constituents
Carnotite	0.355% U	SiO ₂ , Al ₂ O ₃
Uraninite	0.318% U	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , MgO
Torbernite	0.265% U	SiO ₂ , Fe ₂ O ₃
Pitchblend Ores	119-4469 ppm U	SiO ₂ , Al ₂ O ₃
NBL Samples	10 ppm - 1% U	SiO ₂ , MgO
Thorium Samples		
Monazite Sand	8.55% Th	SiO ₂ , rare earths
Chinese Mineral	70 ppm Th	SiO ₂ , Al ₂ O ₃
Sediments/Soils		
NBS River Sediment	1.6 ppm Th, 1.1 ppm U	SiO ₂ , Fe ₂ O ₃
NBS Estuarine Sed.	(10 ppm Th)	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃
Urban Particulate	(7.4 ppm Th) 5.5 ppm U	SiO ₂ , sulfate, Al, Fe
Soil		SiO ₂ , Fe ₂ O ₃ , Al ₂ O ₃ , Mg
Metals		
ALCOA Aluminum		Al
Brass		Cu, Zn
Zinc		Zn
Ceramics		
RR3 Glass Sample	1.83% U	SiO ₂ , B ₂ O ₃ , Na ₂ O, Fe ₂ O ₃

Figure 1. A schematic diagram of the remote LA-ICPAES concept.

Figure 2. An optical spectrum of U and Th at a concentration of 100 ppm each in Fernald soil. The spectral line of Si, the internal reference element is shown.

Figure 3. Calibration data plotted for U (top) and Th (bottom) for synthetic standards prepared from a Fernald soil blank.

FIGURES

Figure 1. Comparison of UII 468.91 nm emission viewed with (A) ordinary resolution monochromator (2nd order) [8] and (B) high-resolution monochromator [20].

Figure 2. Partial mass spectrum for pooled urine. Thorium-232 is added as the internal standard. The U-238 observed is from naturally occurring levels in the urine pool [29].

Figure 3. Time-of-flight mass spectrum of approximately 10^8 atoms of Pu-239 observed by RIMS. No molecular Pu is observed [44].

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