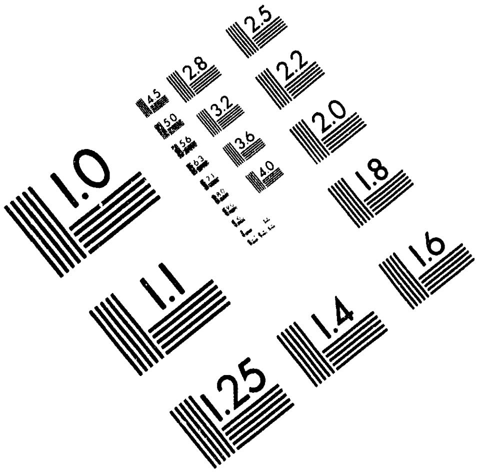

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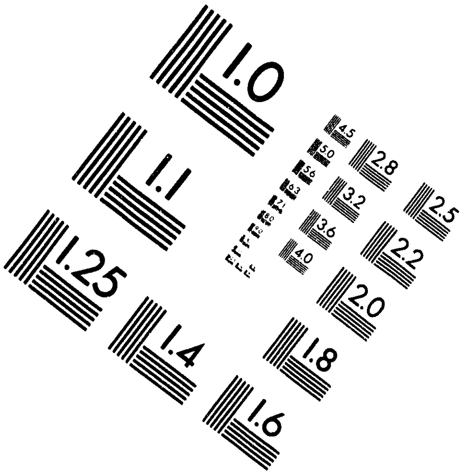

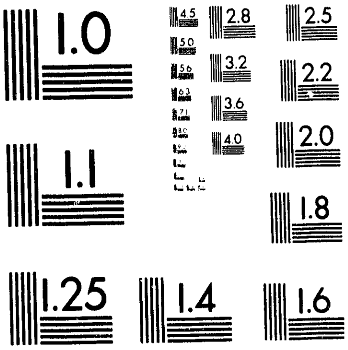

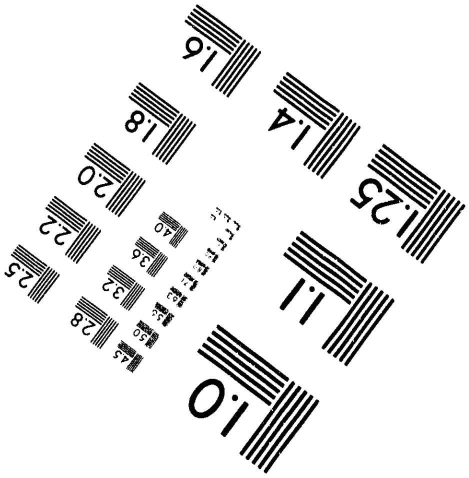

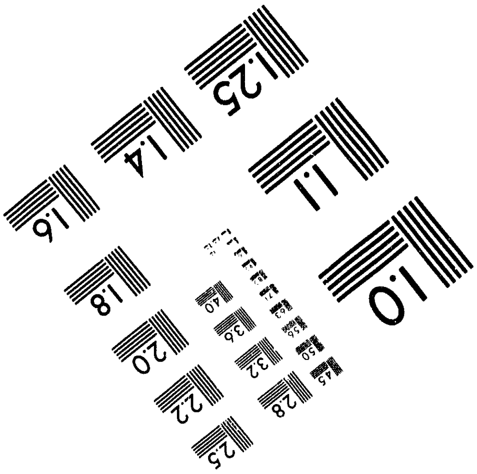

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Laser Ablation ICP-Mass Spectrometry Determination of Th^{230} in Soils at the Gunnison, Colorado UMTRA Site

Report Date
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SUMMARY

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) directly determined the Th^{230} activity levels in 29 soil samples, at the rate of a few samples per hour. The ELAN 5000 ICP-MS, on loan from the Perkin-Elmer Corporation, had the sensitivity necessary to determine the Th^{230} activity at the remediation level, 15 pCi/g (0.8 ppb (ng/g), required by the UMTRA program. The ICP-MS analyzed samples while installed and operated in the completely self-contained *mobile demonstration laboratory for environmental screening technologies* (MDLEST) at the UMTRA site. The direct analysis of soil samples by LA-ICP-MS on-site offers a more rapid turn-around time than is currently being achieved using a conventional off-site laboratory.

A critical comparison of results from different laboratories can only be made if the same soil standards are analyzed by each laboratory; this was not the case at Gunnison since soil standards were not included in the samples sent to the off-site laboratory for analyses. However, a comparison of the mobile LA-ICP-MS and off-site laboratory results indicates that for 20 of the 29 samples analyzed, the two laboratories agree as to whether the Th^{230} activity is above or below the remediation level of 15 pCi/g. While the Th^{230} activity values reported by the two laboratories differ, the results are useful for making decisions concerning the adequacy of the remediation performed. It is not clear whether these differences in activity value are the result of different sample introduction and analysis techniques, or whether there is a systematic error in one of the techniques.

This demonstration showed that a standard production-model ICP-MS is sufficiently rugged to be installed in a completely self-contained mobile laboratory, be transported across the country, and after arrival at the site, be operationally ready to acquire data in a few hours. The system operated in the field for nine days, under winter conditions (as low as -4° F), without a catastrophic failure. Although in situ sampling was not demonstrated due to poor weather conditions, a *global positioning system* (GPS), recently integrated into the MDLEST to acquire satellite information in real-time for mapping in situ sample sites, was demonstrated.

The Ames Laboratory team installed and integrated the ICP-MS into the MDLEST, and had been operating it with the laser ablation sample introduction system for approximately two weeks prior to the Gunnison demonstration. An additional three weeks of operating experience was gained

earlier, while the instrument was installed in a fixed laboratory setting. The schedule for the demonstration required that the demonstration be completed as soon as possible, with the major constraint being the weather conditions that could be encountered in the mountains at the Gunnison, Colorado site during November.

In summary, this demonstration shows the viability of performing rapid, on-site analysis of radioisotopes in soils using LA-ICP-MS as an alternative to the current several-week analysis using an off-site laboratory. Given the constraints and severe weather condition under which this demonstration was performed, the results are encouraging. Additional funding; will support the development of protocols to improve the accuracy of the LA-ICP-MS results, sample preparation methods that will enhance laser ablation particle generation to increase and stabilize the particle stream to the ICP-MS, explore alternative sampling methodology to increase operational efficiencies, and modifications to move the sampling probe inside the MDLEST for efficient sample handling and decrease turn-around time. These developments are suggested to provide a state-of-the-art analytical system, with rapid analysis capabilities, to help UMTRA and other DOE programs to effectively fulfill their remediation requirements.

INTRODUCTION

The Gunnison, Colorado *Uranium Mill Tailings Remedial Action*, UMTRA, site contains a uranium mill tailings pile that is the leftover residue after the extraction of uranium ore, which was mined in the near-by mountains from 1958 to 1962 for national defense purposes. The mission of the UMTRA program is to return the site to its original condition prior to the uranium milling operation. The mill tailings pile is being moved to a new long term (1000 years) storage site, away from the populated area. After the tailings pile has been removed and the soil level is at the original grade, soil samples are taken and analyzed for radium-226 (Ra^{226}) activity. Any soil with a Ra^{226} activity greater than 15 pCi/g, is removed and taken to the storage site. The radium remediation is usually accomplished by removing the top twelve inches of soil. Next, the soil is resampled to determine the thorium-230 (Th^{230}) activity, and any soil where the activity is greater than 15 pCi/g is removed and taken to the storage site. The remediation operation removes six inches of soil at a time followed by resampling to determine the Th^{230} activity, and when the 15 pCi/g level is reached the remediation is complete. The Th^{230} remediation can require soil removal as deep as ten feet below the original site grade. The next stage of the clean-up requires clean soil to be hauled to the site to restore the soil level back to the original site grade.

The analysis of the samples for Th^{230} activity, by an off-site laboratory, is currently taking three weeks to obtain the analytical results. Remediation decisions cannot be made without this information. The UMTRA program has a need for an analytical system that can rapidly detect and accurately determine the amount of Th^{230} in soil samples.

The main objective of the Gunnison demonstration, described in this report, was to evaluate the suitability of the *laser ablation-inductively coupled plasma-mass spectrometry* (LA-ICP-MS) technology operated in a mobile configuration, to satisfy the UMTRA program's needs to quantify Th^{230} levels in the soil for compliance with the Nuclear Regulatory Commission (NRC) agreement of 15 pCi/g. The LA-ICP-MS sampling and analysis technique was chosen because of the capability for rapid analysis, approximately three samples per hour, with minimal sample preparation.

This program was divided into the following tasks:

- Locate and borrow an ICP-MS instrument capable of detecting Th^{230} at the level needed to satisfy the NRC remediation agreement.
- Initially install the instrument in a standard laboratory for check-out, to gain operator familiarity and proficiency in the detection of sub-ppb levels of Th^{230}.
- Prepare the *Mobile Demonstration Laboratory for Environmental Screening Technologies* (MDLEST) system for installation and integration of the ICP-MS.

- Check-out the complete MDLEST/LA-ICP-MS in the shop (using shore power) and locally under field conditions (using diesel generator power).

- Compare the results for samples analyzed using the LA-ICP-MS in the shop and under field conditions while installed in the MDLEST with the results obtained while the instrument was located in the standard laboratory setting.

- Write the demonstration plan for the Gunnison, CO, UMTRA site.

- Transport the MDLEST to the demonstration site at Gunnison, CO.

- Demonstrate the LA-ICP-MS/ MDLEST at Gunnison and analyze the samples provided by the site.
- Return the MDLEST to Ames Laboratory.

- Report the demonstration results.

TECHNOLOGY SCOPE

The Ames Laboratory LA-ICP-MS project was designed to detect Th^{230} and possibly Radium-226 (Ra^{226}) in soil matrices at concentrations of 0.05 to 1000 ppb (ng/g of soil) using in situ field sampling techniques, or having the samples brought to the MDLEST for analysis. The system includes the MDLEST which houses the instrumentation and utilities necessary to support the LA-ICP-MS in the field.

The focus of the site demonstration is to operate the LA-ICP-MS in a mobile laboratory, and quantitate the Th^{230} activity remaining in the soil after the uranium mill tailings have been removed. The ICP-MS is capable of detecting more than 70 elements in a variety of sample matrices. The complete sampling and analysis procedure takes approximately 20 minutes per sample. A microwave oven is available in the MDLEST to dry samples prior to laser ablation if they are too wet for adequate particle generation. The detection limit for Th^{230} needed to satisfy the NRC remediation agreement is 15 pCi/g (~0.80 ppb (ng/g)).

METHODOLOGY AND APPROACH

DEMONSTRATION PLAN

The Gunnison site was visited for a day-and-a-half during October to obtain a copy of the site health and safety plan, and collect the information required to write the site demonstration plan. During this visit the site was surveyed to determine if in situ *Laser Ablation* (LA) sampling was possible in the contaminated area during the demonstration. Two factors at this site enter into the decision to demonstrate the in situ sampling capability, gravel and rocks either buried or on the soil surface and the weather. First, a clear area approximately 12" square, free of rocks, stones (greater than 1/8 inch in diameter), and vegetation, is needed for the sampling probe adapter to sit flat on the ground and penetrate the soil approximately 2" deep. Since the site is covered with soil that contains fine gravel through cobblestones, it will be difficult to find a clear area large enough to set the sampling probe adapter and penetrate the required depth. The second factor is the weather. The demonstration is planned to start November 8 and continue through November 19. This time of year could present a problem with frozen ground and snow cover. Neither of these obstacles was encountered during the earlier demonstration of the in situ sampling technique at the Fernald, OH site. Thus, flexibility was written into the demonstration plan to allow decisions concerning the demonstration of in situ sampling to be made during the demonstration.

Prior to the demonstration the Health Physics Group in charge of sampling at the site, gathered approximately 40 samples that were sent off-site to a conventional laboratory for preparation and analysis. The sample soil preparation involved drying, grinding, sieving, and homogenizing. When these samples were returned to Gunnison, a portion of each sample (~10 g), was loaded into a labeled polypropylene container for LA-ICP-MS analysis.

INSTRUMENT LOAN

The instrument used for sample analysis during the demonstration was an ELAN 5000 ICP-MS obtained on-loan from the Perkin-Elmer Corporation. A preliminary laboratory feasibility study showed the capabilities of this instrument to detect the necessary Th^{230} levels, 15 pCi/g (0.8 ppb), in soil to satisfy the UMTRA remediation agreement.

LASER ABLATION

The LA technique is used for direct sampling of soil. Laser radiation focused on the soil surface generates sample particles that are micron (μm) size. The ablated sample particles are entrained in argon gas that is flowing through the ablation cell, transported through a 20 meter tube, and introduced into the ICP for excitation. This technique eliminates the lengthy, approximately eight-hour, sample dissolution and separation process needed to prepare a sample for analysis. LA has been successfully used for the direct sampling of metals and ceramics.

ICP-MASS SPECTROMETRY

ICP-MS is a technique used to obtain rapid multi-element quantification of samples. The sample is introduced into ICP torch where the high temperature plasma, 8000 K, vaporizes, atomizes, and ionizes it. The ions in the ICP plasma are introduced into the mass spectrometer where they are separated by mass and their intensity (number) is summed. The ICP-MS is capable of detecting elemental ions at the sub-ppb (ng/g) level. This feature makes the ICP-MS a valuable tool for the rapid detection of trace amounts of radioisotopes in the presences of larger amounts of other radioisotopes or heavy metals that might be in the sample and cause interferences for other measurement techniques.

MDLEST OPERATION

The MDLEST is a completely self-contained mobile laboratory. Computers and control systems, electrical power, water, gases, and other utilities required to operate the LA-ICP-MS instrumentation are supplied by the MDLEST. In addition, a newly acquired Global Positioning System (GPS) is installed in the MDLEST to supply real-time coordinate information for mapping in situ sampling sites. The instrumentation and equipment installed in the MDLEST is under computer-control for system monitoring and actuation, and data acquisition and reporting. Thus, the operators have a minimal number of "manual tasks" to perform during the sampling and analysis operation.

The laser used for ablation sampling (Continuum model NY81-30 Nd:YAG laser, 30 Hz repetition rate, and 1064 nm wavelength with frequency doubling and tripling capabilities) is located in the MDLEST. A fiber-optic cable (600 µm core diameter silica fiber, 25 meters in length - Polymicro Technologies model FVP-600660690) transmits the laser radiation (~5.5 mJ) to the sampling probe. The fiber-optic cable is one component in the 20 meter umbilical connection the MDLEST and the sampling probe. The umbilical also contains the aerosol transport tube, the power and control wiring for the electronic systems in the sampling probe, and the GPS antenna wire. The sampling probe is equipped with a GPS antenna for locating in situ sampling sites, the ablation cell that is mechanically sealed to the soil surface, and the mechanism that focuses and rasters the laser beam over the soil surface. Argon gas flowing through the aerosol transport tube carries the ablated sample particles from the ablation cell to the ICP, an integral part of the ELAN 5000 ICP-Mass Spectrometer. A GPS receiver (Ashtech model M-XII), connected to the antenna on the sampling probe, is located in the MDLEST to acquire in situ sample site information.

SAMPLING PROCEDURE AND DATA ACQUISITION

The samples analyzed by the LA-ICP-MS instrumentation at the Gunnison site were supplied by the site Health Physics Group in labeled polypropylene wide-mouth bottles compatible with the LA sampling fixture. These bottles had been initially prepared by placing a large rubber stopper in the bottom so that only 10 grams of sample was needed to fill the bottle to the level required for LA sampling. During the demonstration these bottles were manually placed into the sampling fixture, and the surface sampling probe was set into the fixture over the sample.

Five replicate measurements were acquired by the mass spectrometer during one continuous ablation of each sample covering approximately 1 in^2 of surface area. During each replicate, ion intensity data were acquired for the following elements: Ra^{226}, Th^{230}, Th^{232}, U^{238}, C^{13}, Na^{23}, Mg^{24}, Al^{27}, Si^{29}, K^{39}, Ca^{44}, Ti^{47}, and Fe^{57} and mass 229. Analysis and quantification of these elements were performed rapidly by the ICP-MS instrument software.

CALCULATIONS

After the MDLEST was set up at the Gunnison site, checked-out, and was operating satisfactorily, data were acquired for the three Nuclear Reference Materials (NRM) soil standards, and the results were used to determine a calibration curve. This calibration curve was used for quantification of Th^{230} in the Gunnison samples.

QUALITY ASSURANCE

The instrumentation and equipment in the MDLEST were operated in accordance with the manufacturer's recommendations and safe operating practices.

Conventional nebulization of solution standards was used to check the performance of the ICP-MS analysis system for instrument sensitivity, mass calibration, and resolution. During LA sampling, commercial soil Standard Reference Materials (SRM) and Nuclear Reference Materials (NRM) were used to calibrate the LA-ICP-MS instrumentation. Sources for these reference materials include NIST (SRM 1646, 2704, 4353, and 4355) and UNC Geotech[1] for the NRM samples. The NRM standards, NRM-4, NRM-5, and NRM-6, with certified Th^{230} activities of 13.5, 25.5, and 49.7 pCi/g, respectively, were prepared by the Technical Measurements Center at Grand Junction, CO, for use by remedial action contractors and cognizant Federal and State agencies. The NRM reference materials were prepared by blending mill tailing materials, ores, and a river-bottom soil diluent.

RESULTS AND DISCUSSION

LABORATORY OPERATION

The climatic conditions at the Gunnison site were challenging to both equipment and personnel. During the first week of on-site operation, November 8 - 11, there was no snow on the ground. The temperature ranged from 2° F in the mornings to mid 40's during the afternoons. Overnight on November 11, four inches of snow fell on Gunnison and remained during the rest of the demonstration, through November 20. The temperature during this time ranged from -8° F in the mornings to mid-teens during the afternoons. The Gunnison site did not have the proper electrical power available (3 phase, 208 VAC) to operate the MDLEST from shore power. Thus, the on-board diesel generator supplied the electrical needs of the MDLEST. The decision was made to shut down the generator each evening so that a person would not have to remain at the site all night to monitor its operation. To prevent the MDLEST from completely freezing up overnight, portable electric heaters plugged into 110 VAC site power were used to maintain the temperature between 40° and 50° F in several compartments where various pieces of equipment were located. One morning the space heater in the ICP-MS compartment failed, and the temperature was low enough to freeze the water in the ultrasonic bath sitting on top of the ICP-MS. This lower than normal compartment temperature only extended the start-up time of the ICP-MS by one-half hour, after which it was operating satisfactorily and ready to acquire data.

Following are several examples of field engineering that was necessary to complete the demonstration. The sample probe attached to the end of the umbilical was operated outside of the MDLEST in the harsh weather during the entire demonstration. The sample probe was kept outside of the MDLEST intentionally to prevent contamination of the instrumentation laboratory. The low temperatures in the mornings required the front panel from the sampling probe to be removed so that a heat gun could be used to warm up the stepper motors of the rastering system. After the stepper motors attained operating temperature they were able to adequately maintain the temperature in the probe. During mid-afternoon if the sun happened to shine on the black plastic cover on the side of the sampling probe, the temperature in the probe housing rose above the normal operating temperature and affected the operation of the electronic control system. This problem was solved by simply moving the sampling probe into the shade of the MDLEST. The first morning at the site, the laser and ICP-MS would not operate. The problem was traced to the system that supplies cooling water to these instruments. The water temperature was below the minimum operating temperature for the instruments. A tank heater, bypass line, and control valve were installed to warm and regulate the cooling water so that the proper operating temperature (20° C) could be reached quickly. These problems were solved in the field, allowing the demonstration to continue.

Before leaving the Gunnison site, the Health Physics Group surveyed areas in the MDLEST, instrumentation, and equipment that could possibly have been contaminated during the demonstration. Areas of specific concern were the sample transport tube connecting the ablation cell to the ICP. This tube was back-flushed into a cleaning box specially designed with a High Efficiency Particulate Air (HEPA) filter for this purpose, using high pressure argon gas to remove any sample residue that may have settled out during the sampling process. This sample residue was surveyed and did not contain any radioactive contamination above site background levels. The ICP-MS instrument, the compartment where it is located, and the HEPA filter, located approximately 1 meter above the chimney of the ICP, were surveyed, and only background levels of activity were present.

In situ sampling was not demonstrated at Gunnison due to poor weather conditions. However, the Global Position System (GPS) instrument that has recently been integrated into the MDLEST to acquire satellite information in real-time for mapping in situ sample site location was demonstrated.

DATA PROCESSING

Quantification of Th^{230} was performed during the demonstration by the ICP-MS software. These results were used to provide immediate instrument performance feedback and an indication of the amount of the Th^{230} present in the Gunnison samples analyzed. The results reported, later in this report, are the re-analysis of the raw intensity data.

SAMPLE PRECISION

As described in the sampling procedure, data for five replicate measurements were acquired for each sample. It was noticed that the intensities for the first two replicates on the first two days were lower than the last three replicates. This was traced to having an insufficient delay time between starting sample ablation and starting data acquisition by the ICP-MS. This problem was solved by increasing the delay time between the starting of these two operations. Thus, in order to use the data acquired on the first two days, the last three replicates of each sample were used to determine the mean intensity. After the delay time was lengthened, all five replicates were used to determine the mean intensity for a sample.

After the first two days of the demonstration, Ra^{226} intensities were evaluated and it was evident that the instrument was not sensitive enough to detect the radium isotope at the 15 pCi/g (.015 ppb) level that is necessary to satisfy the UMTRA remediation level. After this evaluation, no additional Ra^{226} data were acquired. However, the ICP-MS has the sensitivity necessary to determine the Th^{230} activity at the 15 pCi/g remediation level required by the UMTRA program.

INTERNAL STANDARDIZATION AND DATA ANALYSIS

Argon intensities, in the absence of an ablated sample, were acquired several times during the demonstration. These intensities were to be used to correct the mass intensities for any effects caused by the argon in the ICP plasma. Examination of these intensities showed a large contribution at mass 29, the silicon mass, in the absence of an ablated sample. Since the plasma intensity can not be separated from the mass 29 intensity, all acquired argon background intensity data are ignored and the total mass 29 signal is used for internal standardization.

The intensity measured at mass 230 is quite small and is comprised of two signals, the ions attributed to the Th^{230} in the sample plus a small background contribution. This small background contribution is thought to be independent of the sample composition and therefore is constant over nearby masses. Thus, the sample protocol included acquiring data at mass 229 to correct the results at mass 230 for background effects. The corrected Th^{230} intensity is determined by subtracting the mass 229 intensity from the mass 230 intensity. Finally, the corrected Th^{230} intensity is ratioed to the mass 29 intensity and the result is used with the instrument calibration curve to quantitate the Th^{230} activity level of the unknown samples.

LA-ICP-MS INSTRUMENT CALIBRATION

The relationship of the Th^{230}/ mass 29 intensity ratio and the Th^{230} activity was determined using LA-ICP-MS data obtained for the three NRM reference samples (described under quality assurance above). These measurements were made after the MDLEST was first set up at the Gunnison site and the instrumentation was operating satisfactorily. The data were plotted on the graph and then fit with a linear least squares representation. The curve was forced to pass through zero. Figure 1 shows the Th^{230} calibration curve for NRM data collected. The data points are the mean value of the intensity ratio and the error bars are the standard deviation of the replicates. The Th^{230} activity for all of the samples was calculated using this calibration curve.

CALCULATING SAMPLE ACTIVITY

The NRM-5 standard sample was analyzed every few samples during the demonstration as a monitor to determine the consistency of the measurements and the operation of the sampling system and mass spectrometer. These results were used along with the calibration curve in Figure 1 to quantitate Th^{230} in the unknown samples. Figure 2 shows the NRM-5 Th^{230}/ mass 29 intensity ratio measured over the course of the demonstration. The data points are the mean value of the intensity ratios and the error bars are the standard deviation of the replicates. The scatter in the intensity ratio for this standard sample makes quantification of the unknown samples difficult. These differences are probably caused by any one or a combination of fluctuations in laser ablation, sample transport, or ICP-MS instrument sensitivity. To use the NRM-5 data to calculate the Th^{230} activity for an unknown sample, the assumption was made that the difference in the reference value (25.5 pCi/g) and the calculated value, obtained using the calibration curve, represents a change in the system response that will be the same for an unknown sample analyzed near the same time. Thus, the Th^{230} activity for an unknown sample was determined by using the calibration curve to calculate the activity for the sample's Th^{230}/ mass 29 intensity ratio and correcting this value using the NRM-5 reference activity (25.5 pCi/g) divided by the immediately

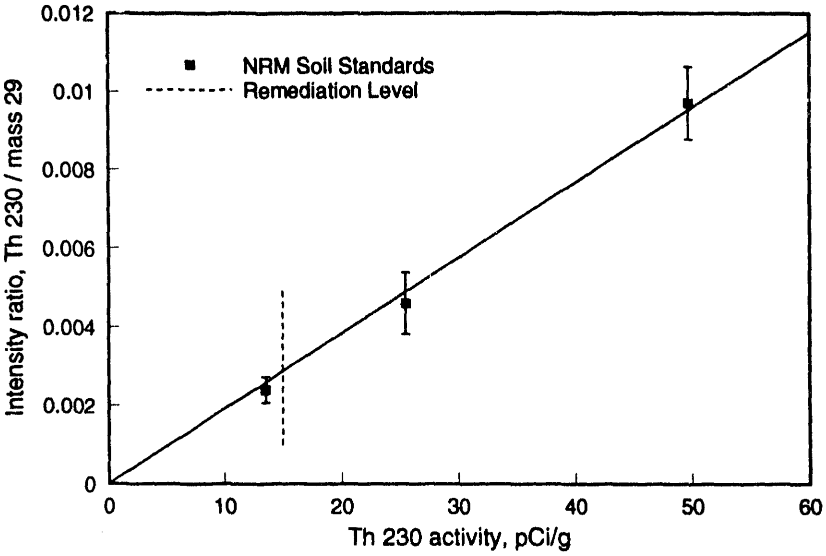

Figure 1. Th^{230} Activity Calibration Plot Showing the LA-ICP-MS Calibration Curve and the UMTRA Remediation Level

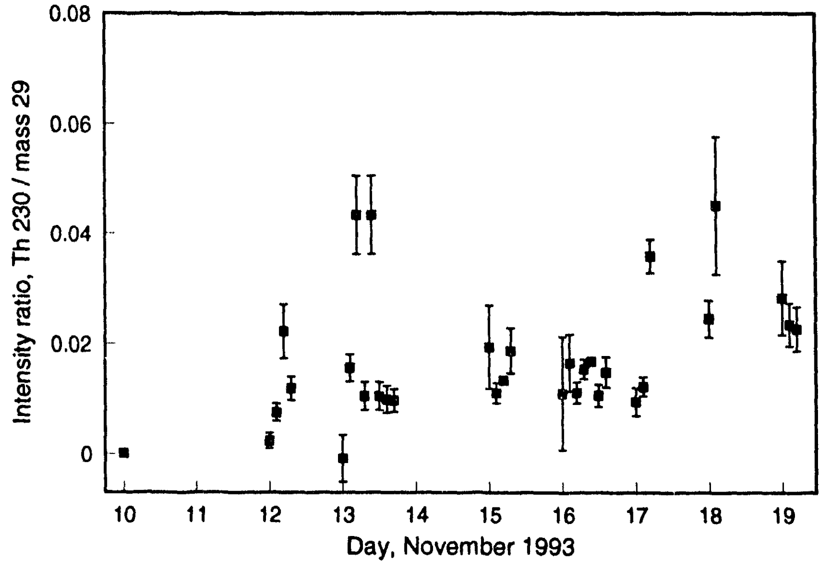

Figure 2. Variations of NRM-5 Intensity Ratio During the Demonstration

preceding NRM-5 determined activity.

After the ablation of a number of samples the orifice in the sampler and skimmer cones in the mass spectrometer became sufficiently coated with sample residue to prevent ions from entering the mass spectrometer for analysis. The NRM-5 results and the vacuum pressure in the mass spectrometer were used to determine when the orifice was sufficiently plugged and required cleaning. The orifice in these cones was cleaned at start-up each morning and during the day as needed using an ultrasonic bath. Sometimes the day-time cleaning was done by simply wiping the cones off with a Kimwipe. An NRM-5 sample was usually run just prior to cleaning the cones, and it was the first sample run after the spectrometer was ready to acquire data again, so the consistency of the results could be tracked. The points in Figure 2 with large error bars are usually the first point of the day or the first point taken after cleaning the cones. The large deviations and apparent NRM-5 intensity offset shown for November 18 and 19, different from the results on the preceding days, are not understood. While trying to understand this shift in the calibration is important from an instrumentation standpoint, it is not critical to the particular data involved as long as it is recognized that the calibration has changed and this change is taken into account. It is important to remember that the quantitation of unknown samples is related directly to the comparison with the NRM soil standards.

The intensity ratio of mass 229, a small signal used to monitor the background level, to mass 29, a relatively large signal, should be a good monitor of the ablation sampling process, the sample aerosol transport, the ICP ionization system, and the mass spectrometer sensitivity to low mass elements. Figure 3 shows the mass 229/ mass 29 intensity ratio for NRM-5 during the demonstration. This Figure shows that mass 29, a light mass, containing the combined Si^{29} and background intensity is resolved with similar precision and the results show similar scatter as seen in Figure 2 for Th^{230}. The points in Figure 3 with the large error bars are usually the first run of the day after cleaning the cones and are erratic similar to the results seen in Figure 2. The NRM-5 standard was always run at the beginning of the day, and sometimes it was run twice before any unknown samples from the site were run. This could be a source of

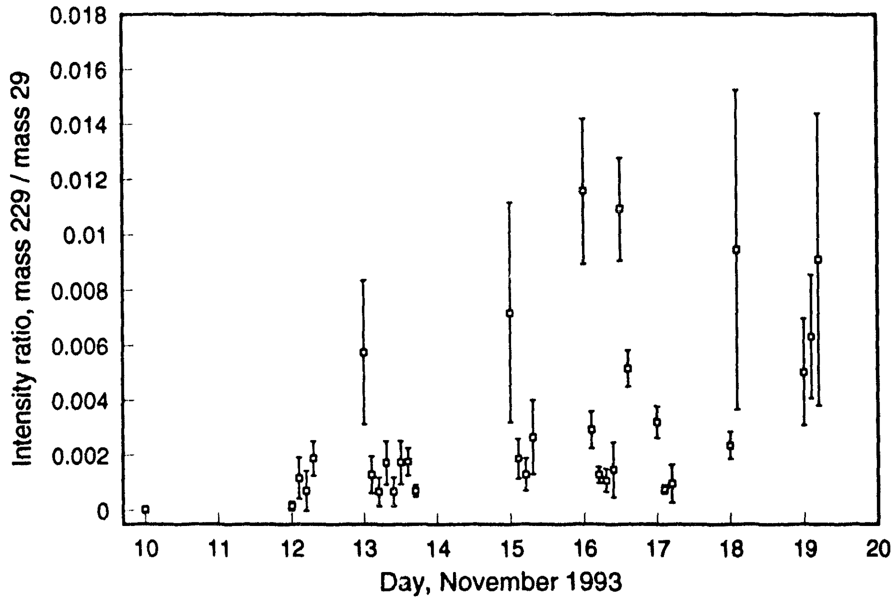

Figure 3. Variations of Mass 229/ Mass 29 Intensity Ratio for NRM-5 During the Demonstration

error in the quantitation of the site sample. Again, as seen in Figure 2, the data on November 18 and 19 are erratic, and the reason is not understood.

ANALYTICAL RESULTS

The activity values (pCi/g) for the Gunnison samples analyzed during the demonstration are given in Table I along with the standard deviation for the measurement. While it is easy to linearly extrapolate the calibration curve shown in Figure 1 to very large Th^{230}/ mass 29 ratios to determine the Th^{230} activity, it must be cautioned that only values of the ratio equal to or less than 9.53×10^{-3} can be stated with any confidence. This maximum Th^{230}/ mass 29 intensity ratio is the value determined from the calibration curve for 49.7 pCi/g, the NRM-6 soil standard activity. The values of the Th^{230} activity that were determined by extrapolating the calibration curve are identified in Table I with a (†). Comparison of LA-ICP-MS analysis of the Gunnison samples with results obtained using conventional sample introduction or radiochemical techniques are meaningful only if the same NRM standards also are used. Analyzing the same standards by the various methods will identify systematic calibration differences and possible instrumentation and sample introduction problems between the different measurement techniques.

The Gunnison samples were previously analyzed by an off-site laboratory using conventional dissolution and radiochemical techniques. The analyzed results from this laboratory were supplied by the Gunnison Health Physics Group and are shown in Table I. During our demonstration, a trailer containing a Th^{230} wet-chemistry laboratory was being set up on the Gunnison site to analyze soil samples locally on-site. After this on-site laboratory was operating, several samples that had been analyzed using LA-ICP-MS were provided to this laboratory for analysis, including the NRM soil standards. The preliminary results from this on-site laboratory are being evaluated, and have not been included in this report for comparison.

Comparing the LA-ICP-MS and off-site laboratory results given in Table I, both analyses agree that 8 of the 29 samples analyzed have Th^{230} activities that are greater than the 15 pCi/g remediation level, and that additional remediation of the area where these samples were taken is required. Both analyses agree that twelve additional samples have Th^{230} activities that are less than the remediation level, indicating that remediation is completed in the areas where these samples were acquired. The results for the remaining 9 samples are not in agreement. The LA-ICP-MS values are greater than the 15 pCi/g remediation level, while the off-site laboratory values are less than the remediation level. In general, whether the results from both analyses agree or not, the LA-ICP-MS values are usually high relative to those reported by the off-site laboratory, by more than an order of magnitude in some cases. This observation does not depend on the result being either above or below the remediation level.

Some of the samples were re-analyzed several times to determine the consistency of the results. Usually these repeat analyses were performed on different days. For sample C-4-11 16, three of the six determinations were performed in succession on the same day. The Th^{230} activities determined for the repeat analyses vary by a factor of two to three for some of these samples. The uncertainty in Th^{230} activities for the repeat analysis does not show values large enough to account for the

Table I. Sample Th^{230} Activity Values

Sample ID	LA-ICP-MS Results Mean pCi/g	LA-ICP-MS Results Std Dev pCi/g	Off-Site Laboratory pCi/g
0002 sta1	526†	19	190.0
0003 sta4	22	7	0.1
0013 sta9	369†	17	
0013 sta9	510†	22	190.0
0013 sta9	476†	29	
A-31-17 26	1	1	0.8
A-31-17 26	8	3	
A-39-24 28	410†	10	20.0
A-46-11 30	503†	7	80.0
A-46-16 29	704†	47	68.0
B-11-25 20	1	3	1.4
B-12-23 22	5	3	2.2
B-12-23 22	5	3	
B-25-7 23	18	2	2.4
B-37-1 24	10	2	3.0
C-20-1 14	4	1	2.2
C-3-14 17	140†	11	9.3
C-3-15 18	124†	6	13.0
C-4-11 16	75†	13	
C-4-11 16	40	12	
C-4-11 16	81†	6	8.4
C-4-11 16	78†	4	
C-4-11 16	27	2	
C-4-11 16	68†	5	
C-4-12 15	15	3	3.5
C-5-13 13	6	6	2.0
D-14-25 32	5	2	1.1
D-14-25 32	5	2	
D-15-23 33	9	2	1.3
D-31-17 35	86†	3	
D-31-17 35	41	5	2.7
D-31-17 35	45	8	
D-35-20 39	267†	7	29.0
D-38-4 31	4	2	0.8
D-43-15 36	10	22	9.2
D-43-20 37	111†	12	17.0
E-2-13 40	4	2	2.9
F-11-24 4	35	2	4.2
F-11-5 10	765†	31	40.0
F-27-4 6	8	1	7.7
F-28-13 2	18	9	2.1
GRN GT	6	5	
NIST 2704	-2	3	
NIST 2704	2	0	
NIST 1646	0	3	
NIST 4355	-2	2	

* Nuclear Reference Material Standard Soils with certified Th^{230} activities (pCi/g)

NRM-4 * 13.5
NRM-5 * 25.5
NRM-6 * 49.7

† These Th^{230} activity values were determined by extrapolating the calibration curve to values greater than 49.7 pCi/g, the NRM-6 soil standard value. Values greater than 49.7 pCi/g have a have a lower level of confidence.

differences seen between the mean activities. These large differences in the repeat analyses indicate possible variations in the laser ablation sampling or changes in the ICP-MS response that were not adequately compensated for in the data analysis.

The five samples listed near the end of Table I, GRN GT and the NIST reference soils, have not been contaminated by uranium tailings. The GRN GT sample was taken near the entrance gate at the Gunnison site. These samples are not expected to have Th^{230} activity values above the background levels. These samples were analyzed to gain information of the potential for a false positive Th^{230} reading. The results from these samples also indicate that it was unlikely that any cross-contamination occurred among any of the various samples using the same 20 meter aerosol transport tube.

CONCLUSIONS

The LA-ICP-MS results reported in Table I show that this technique has the sensitivity necessary to determine Th^{230} activity at the remediation level, 15 pCi/g, required by the UMTRA program. Direct analysis of soil samples by LA-ICP-MS in a mobile laboratory at the site allows a few samples per hour to be analyzed to determine the Th230 activity level, which is a more rapid sample turn-around time than is currently achieved using conventional off-site laboratories. A comparison of the LA-ICP-MS and off-site laboratory results indicates that for 20 of the 29 samples analyzed, the two laboratories are in agreement as to whether the Th^{230} activity is above or below the remediation level. Although the Th^{230} activities reported by the two laboratories differ, the results are useful for making decisions regarding the adequacy of the remediation performed. It is not clear whether the differences in the values are the result of different sample introduction and analysis techniques, or whether there is a systematic error in one of the techniques. As described in the Analytical Results section, the uncertainty in the LA-ICP-MS results presented in Table I can be judged by the variation in the repetitive analyses performed for some of the samples. It is difficult to judge the accuracy of the off-site laboratory values reported in Table I since there is no indication of the uncertainty in the results, and no determination of certified standard reference samples. A critical comparison of results from different laboratories can only be made after the same soil standards have been analyzed by each.

This demonstration has shown that a standard production-model ICP-MS is sufficiently rugged to be installed in a completely self-contained mobile laboratory, be transported across the country, and after arrival at the site, be operationally ready to acquire data in a few hours. The total system operated in the field for nine days, during winter conditions, without a catastrophic failure. The ICP-MS sensitivity measured in Gunnison was less than measured in Ames before the trip. Inspection of the mass spectrometer did not reveal the cause of this sensitivity loss. However, the sensitivity of the ICP-MS at Gunnison was adequate to determine Th^{230} at the 15 pCi/g (0.8 ppb) remediation level required by the UMTRA program. After returning to Ames, during cleaning of the ion optics in the mass spectrometer, an electrical connection to one of the lenses was found broken. Repairing the ion lense connection restored the sensitivity of the ICP-MS to the level seen prior to the Gunnison trip. Although in situ sampling was not demonstrated due to poor weather conditions, a GPS system, recently integrated into the MDLEST, to acquire satellite information in real-time for mapping in situ sample sites was demonstrated. Several field engineering tasks were performed during the demonstration to remedy cold weather operating problems, allowing the demonstration to be successfully completed.

The Ames Laboratory team installed and integrated the ICP-MS into the MDLEST and had been operating it with the laser ablation system for approximately two weeks prior to the Gunnison demonstration. Three additional weeks of instrument operating experience was gained using a different laser ablation system while the ICP-MS was installed in a conventional laboratory setting at the Ames Laboratory. Given the time constraints under which this demonstration was performed, the results are encouraging. Additional funding and development will improve the accuracy and reliability of the LA-ICP-MS results and would enable the MDLEST to be modified to enhance the system operation for more effective employment at UMTRA sites.

RECOMMENDATIONS

Additional methods development is needed in order to improve the results obtained from the LA-ICP-MS. Due to time constraints in obtaining, operator training, installing, and integrating the ICP-MS in the MDLEST and the scheduling requirements, a minimal amount of time was spent on developing and testing analytical methodology prior to the demonstration at Gunnison. From experience gained during the demonstration, a number of modifications to both equipment and methods that were used on-site are necessary. These modifications may include: using direct laser ablation of the soil samples; develop sample preparation methods to enhance laser ablation particle generation to increase and stabilize the sample stream to the ICP-MS; explore alternative sampling methodology and protocol to increase operational efficiency; and incorporating a system for measuring the amount of sample that is being introduced into the ICP for analysis.

A set of unknown samples, including standard reference soil, should be circulated in a round-robin to the laboratories for analysis. This would enable a critical comparison of the results from the different analytical methodologies to be made, and would provide insight into the differences seen between the LA-ICP-MS and off-site laboratory results.

If the needs of the UMTRA program are to bring the samples to the mobile laboratory for analysis and not have the in situ capability, then a number of changes to the MDLEST design can be made that will improve the overall system efficiency and operation. The sampling probe would be moved inside the MDLEST and modified for efficient handling of samples to reduce the analysis turn-around time.

These recommendations are suggestions for modifying the current LA-ICP-MS/ MDLEST system to move the technology from a demonstration prototype into an analytical production system to satisfy the analytical needs of the UMTRA program.

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