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A NEW MASS-SPECTROMETRIC FACILITY FOR THE ANALYSIS OF HIGHLY RADIOACTIVE SAMPLES *

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ABSTRACT

A new facility has been completed for the analysis of highly radioactive, gamma-emitting solid samples. A commercial spark-source mass spectrometer was adapted for remote handling and loading. Electrodes are prepared in a hot cell and transported to the adjacent lead-shielded source for analysis. The source was redesigned for ease of shielding, loading, and maintenance. Both solutions and residues from irradiated nuclear fuel dissolutions have been analyzed for elemental concentrations to <1 ppm; isotopic data have also been obtained. This is the first time such highly radioactive samples have been analyzed directly for trace elemental concentrations over a broad range of elements.

INTRODUCTION

This report describes the design and operation of a new facility for the analyses of solids which are too highly radioactive to be handled by conventional methods. Such materials are commonly produced through intense neutron irradiation or fission processes and often cannot be handled in reasonable quantities outside hot cell conditions. Information on hazardous sample types has been badly needed in nuclear fuel burnup studies, in fuel reprocessing chemistry,[1] and in various nuclear experiments. The analyses must include isotopic ratios and quantitative elemental data at trace concentrations.

DESIGN

To satisfy the analytical requirements, we chose to adapt a spark-source mass spectrometer (SSMS)[2] to handle hazardous materials directly. The high-voltage, radio-frequency discharge of the spark source produces an abundance of primarily elemental ions regardless of their previous chemical form, and demonstrates a moderately uniform, high sensitivity for most elements. Since the spark source merely requires a small pair of electrically conducting electrodes for analysis, sample preparation is minimal and lends itself easily to remote handling procedures.

Our experience with another SSMS facility,[2] which is used for analyzing alpha-emitting and low-level beta- and gamma-emitting samples by using glove box containment, revealed that virtually all radioactive contamination stays within the source. Although dilution of samples is a possibility for lowering radiation to levels where shielding is not required, dilution factors of as high as 10^6 have been required and result in a corresponding loss in sensitivity and difficulty with elemental contamination. Other samples in the form of insoluble solids cannot be easily diluted. Therefore, samples are best analyzed directly; shielding will then be required, but need not extend past the source region of the mass spectrometer.

In order to test the feasibility of adapting a mass spectrometer to remote sample handling schemes, a study was undertaken to simulate hot conditions. A plastic box with a master-slave manipulator was mounted to an Associated Electrical Industries MS-7 SSMS. As a result, a number of electrical controls and monitors had to be relocated. Sample loading was accomplished via the manual manipulator; sparking conditions were monitored by closed-circuit television with adjustment of the spark by remotely actuated electrical motors. Several design features necessary in the final instrument were more clearly revealed through the use of this mock-up. For example, the spark source needed to be carefully designed, not only for ease of electrode loading and adjustment, but also to make remote repairs possible. Additionally, by sparking known standards, the study proved that analytical results were not degraded through instrumental modifications.

The completed facility was designed to handle irradiated nuclear fuel solids in which the most significant gamma after aging is that due to ^{137}Cs (0.66 MeV). Due to the high sensitivity of the SSMS, only about 1 mg or less material is required for analysis. Calculations based upon these assumptions showed that about 10 cm of lead would provide the necessary shielding with a considerable safety factor. In fact, hard radiation levels to approximately 100 R/h at contact could be tolerated.

Figure 1 shows a cutaway schematic drawing of the facility, positioned adjacent to a connecting hot cell in the High Radiation Level Analytical Laboratory at Oak Ridge National Laboratory. Solid electrodes containing a small amount of sample are prepared within the hot cell, so that only the electrodes are transferred to the lead-shielded box where they are loaded into the SSMS. With leak-tight construction and necessary shielding, the facility protects the operator from radiation exposure.

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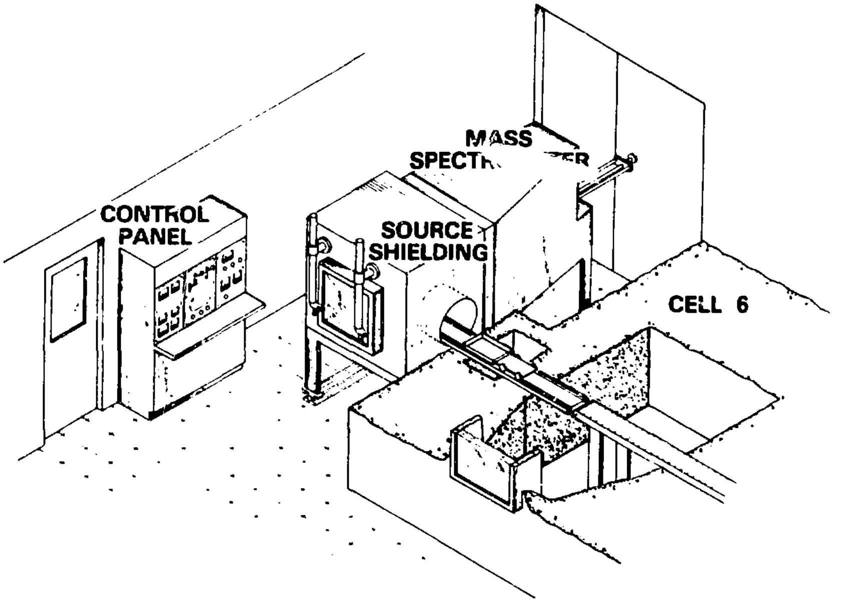

Fig. 1. Schematic, cutaway diagram of the shielded SSMS facility.

Other features of the facility are: a relocation of all control and monitor functions to a remote panel, a leaded-glass view window, an external video camera and remote monitor for observation of the spark, a 20-cm-diameter shielded glove port for entry of source parts, and a continuous, filtered air flow toward the hot cell which insures negative pressure containment.

SOURCE

Due to special requirements of shielding and manipulator sample handling, the spark source needed a radical redesign. The conventional source adjusts the spark gap by means of vacuum interfaced, gimballed micro-manipulators, which are located on the sides of the source annulus. These were relocated to the vacuum viewport, which allowed lead shielding to be packed immediately about the source annulus and also simplified source maintenance.

The electrodes themselves are pressed into graphite blocks which are drilled to accept a banana plug on the ends of the gimballed, insulated posts inside the source. These blocks are easily handled and loaded by means of the master-slave manipulators and can be discarded to reduce contamination. Sheet metal shields are located within the source annulus to collect sputtered or fallen radioactive material. These can be replaced with clean shields when needed (loaded through the cold port). All of the more frequently handled components are mounted on the faceplate, which is retracted on a linear ball bearing and aligned onto the optic axis by dowel pins. The use of easily machinable materials and spot-welded sheet metal parts provides both an economical and a semi-disposable system. A reversible electric screwdriver with interchangeable tips facilitates repair operations. All components are accessible when the faceplate assembly is retracted and rotated to a horizontal position.

OPERATION

Sample electrodes are prepared in the hot cell. Solutions are loaded in the conventional manner by spiking with reference element, such as erbium, and evaporating on the tipped graphite electrodes. Due to the additional handling difficulties involved in hot cell work, we chose a simplified loading technique for insoluble powders. We found very satisfactory spectra could be obtained after pushing a fractured graphite electrode into the powdered sample. Impurity concentrations to less than 50 ppm could be seen. Caution is advised when using this method for powdered samples which are inhomogeneous on a scale of spark crater dimensions (the order of 0.01 mm).

The prepared electrodes (containing only a few micrograms to a few milligrams of solids) are transferred directly to the shielded source region by a small cart and push rod mechanism. Once loaded into the source and a sufficient vacuum (10^{-4}Pa) obtained, sparking is commenced. The electrodes are adjusted by controls at the remote panel with the beam current being monitored for maximum value. Although a tip-to-tip configuration is often used, sparking can be controlled between the sides of the electrodes. Conventional recording of spectra by graded exposures on photoplates is used for ion detection.

DATA ANALYSES

Once the photoplates are developed, they are analyzed on a microdensitometer. Semi-quantitative results can be obtained by visual inspection for the appearance of lines on each exposure and correction by the spiked element intensity, atomic weight, and relative sensitivity factor.

More precise results are obtained by scanning over lines of interest and calculating the background-corrected peak intensity or area by computer. The intensity of each isotope peak is used to calculate an equivalent elemental concentration by ratioing with an internal standard and adjusting for the atomic weight, sensitivity factor, and isotopic abundance. The printout is ordered according to element and mass, and results of different exposures for the same isotope are averaged.

Features of the computer programs are long-term storage of raw data and the ability to recalculate using different isotopic abundance or sensitivy tables. Calculations based upon area comparisons are much more insensitive to focal variations than are those based upon peak intensities. A visual display of each scan allows one to check line profiles and to manually select a background or peak height when necessary (e.g., in the case of a mass multiplet). Exact mass identification can be made following a scan over several amu and the assignment of two reference masses on the scale. An unambiguous determination of the ionic species, whether molecular, or singly- and multiply-charged, results from the measured mass defect which can be determined to within 0.01 amu. These features have been very helpful with unusual sample types, such as highly irradiated material.

ANALYSES OF RADIOACTIVE SAMPLES

Several radioactive solutions and solids have been analyzed in the new facility. The solutions result from acid dissolutions of segments of neutron irradiated, plutonium-uranium fuel rods. Small amounts of precipitates from the acid solutions developed and required direct analysis due to their insolubility. Obviously, a knowledge of composition of these materials is vital to nuclear fuel reprocessing efforts.

A typical mass spectrum of a dissolver solution in the region of the fission product yield is shown in Figure 2. Although the photoplate response is not linear over the range of intensities shown, we can make several interesting observations. First, the classical dual-lobed fission product envelope is apparent and is found to be reasonably consistent with ORIGEN[3] calculations. Second, elemental sensitivity factors are moderately uniform. (Elements such as Cs, masses 133, 135, and 137, and Rb, masses 85 and 87, are obviously enhanced, however.) Third, mass lines around 100 amu are depressed. These were precisely those elements found in abundance in precipitates which fell out of these solutions.

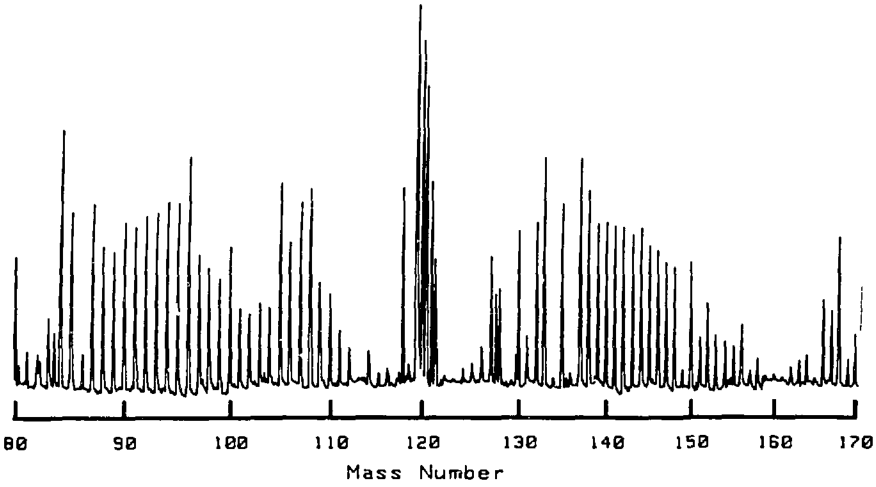

Fig. 2. Mass Spectrum of a dissolution of an irradiated plutonium uranium fuel rod. The ordinate corresponds to photoplate density and is not linear with ion signal.

The precipitates appeared as very fine black powders[1] (0.001 mm to 0.060 mm), with a radiation level of about 1 R/h/mg. Using the electrode loading method described above, analyses were performed in triplicate using various electrode orientations during sparking in an attempt to sample all the material that was loaded. Results indicated very reproducible spectra for most elements. Since no internal standard was available for this material, only ratios of concentrations could be determined. However, by summing the concentrations for those elements heavier than iron (56 amu), an estimate of the total concentration could be made.

Greater than 90% of the spectrum came from Mo, Te, Ru, Rh, Pd, and Ag (95 amu to 110 amu) with an additional 5% being due to a tungsten impurity.

An interesting comparison of the isotopics between the dissolved elements in the solution and precipitate can be made. A noticeable deviation from predicted isotopic abundances was noticed for a few isotopes. For example, there is a noticeable effect for Mo-95 and Pd-106 as shown in Table 1. This type of data can provide clues to the composition and chemistry of the fuel since isotopic fractionation of this magnitude in a mass spectrometer is not possible.

Table 1. Isotopic Abundances of Mo & Pd in Irradiated Fuel

		ORIGEN Calculation	Solution	Residue 1	Residue 2
Mo	95	0.211	0.60	0.052	0.064
	97	0.237	0.13	0.28	0.27
	98	0.252	0.13	0.28	0.29
	100	0.298	0.14	0.38	0.38
Pd	105	0.313	0.48	0.21	0.24
	106	0.288	0.10	0.65	0.55
	107	0.202	0.23	0.087	0.11
	108	0.141	0.15	0.044	0.076
	110	0.040	0.032	0.0077	0.019

CONCLUSION

In our limited experience with the new facility, we have seen results very similar to those obtained with conventional SSMS. Very importantly, however, this is the first time that samples with a high gamma intensity have been analyzed directly for a very broad range of the elements at trace concentrations. The facility is expected to be very useful for the determination of both elemental and isotopic data for a variety of radioactive samples.

Several improvements and additions are planned for the facility. We are in the process of adapting pressed-powder techniques to hot cell use. The solid sample would be ground, powdered, and mixed with a spiked conducting powder, such as graphite or silver, and then, by means of a hydraulic press, formed into a conducting rod. Thus, an internal standard could be provided, and sample inhomogeneity could be reduced when needed. An ion-beam chopper would be useful in reducing effects of inhomogeneity. For rapid determinations with greatly increased precision, electrical rather than photoplate detection is planned. This, coupled with a more stable ion source such as a hollow cathode, could be used to provide more precise isotopic ratios. In fact, the design of the facility allows a variety of ion production techniques to be employed, followed by mass analysis.

Immediate work is planned to improve the accuracy of analyses. The elemental sensitivity factors must be more accurately known for these solids. Checks using prepared standards and isotopic dilution will be made. Additional techniques such as energy dispersive gamma analysis or activation analysis could possibly be used to provide internal standards for these samples.

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