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QUALITY ENGINEERING AND CONTROL
SEMIANNUAL PROGRESS REPORT
NOVEMBER AND DECEMBER 1978 AND
JANUARY THROUGH APRIL 1979

Robert L. Carpenter

Rockwell International

Energy Systems Group
Rocky Flats Plant
P.O. Box 464
Golden, Colorado 80401

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**ROCKWELL INTERNATIONAL
ENERGY SYSTEMS GROUP
ROCKY FLATS PLANT
P.O. BOX 464
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for the
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Atomic Absorption Spectroscopy
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 Decontamination
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 Electrolysis
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 Energy Dispersive X-Ray Analysis
 Gallium
 Gas Analysis
 Gas Chromatography
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 Yttrium

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ATOMIC ABSORPTION SPECTROSCOPY

DISSOLUTION AND ANALYSIS OF PLUTONIUM-IRIDIUM ALLOYS

Donald P. Anderson and John D. Grooms

Summary

A technique for the dissolution of a plutonium-iridium (Pu-Ir) alloy and subsequent analysis of the Ir by atomic absorption (AA) spectroscopy has been developed. Following a peroxide fusion of the sample, the Ir concentration is determined by conventional AA spectrophotometric techniques with a relative precision of ± 15 percent. Accuracy of the method is largely dependent on the fusion technique.

Experimental

Specifications on Pu-Ir alloy required the Ir content to be within the range of 0.09 to 0.11 weight percent. Quality control of this alloy required development of an analytical method for the determination of Ir in the Pu alloy. The relatively small amount of Ir present made AA spectroscopy analysis an attractive choice.

Normal acid dissolution of the alloy for AA analysis was not possible because of the insoluble nature of the Ir. Therefore, wet chemistry facilities were used to adapt a fusion method¹ to solubilize the Ir.

The Pu metal sample is dissolved in 6 normal (N) hydrochloric acid (HCl) and passed through a 0.1 millimicron Millipore® filter. The insoluble Ir is collected on the filter which is then placed in a

nickel (Ni) crucible and ashed in a muffle furnace. A sodium peroxide (Na_2O_2) flux is added to the ash and fused for five minutes at 750°C . The melt is dissolved first in distilled water, then in 6 N HCl, and transferred to a 50 milliliter (ml) volumetric flask. The filtrate from the Pu-HCl dissolution and 0.2 ml of an aqueous solution containing copper (Cu) at a concentration of 200 grams per liter (g/l) are added to the volumetric. The Cu is added to enhance the Ir sensitivity in the AA analysis. The sample is brought to volume with 2 N HCl and is then ready for AA analysis.

The AA standards are prepared to closely match the final sample matrix. A standard Ir solution is made from Specpure® diammonium iridium(IV) chloride, $(\text{NH}_4)_2\text{IrCl}_6$, and is used to spike Ir at various concentration levels into a matrix solution containing 20 g/l Pu, 6 g/l Na, 3 g/l Ni, and 0.4 g/l Cu.

An analysis was performed on several sample solutions to determine the average amount of Ni added to the melt by the crucible during the fusion step. The Ni acts as an absorption suppressant in the AA analysis of Ir and must therefore be closely matched in the standard matrix. The addition of Cu nearly cancels the effect of Ni on Ir absorption.

Samples and calibration standards are aspirated directly into an air-acetylene flame, and Ir absorption is monitored at the 263.9 nm wavelength. The low absorption sensitivity of the Ir necessitates multiple aspirations. Therefore, samples and standards are each run five times and an average value is reported. The precision of the method is ± 15 relative percent. Accuracy has not been determined because of the lack of an alloy standard material, but is dependent on the relative completion of the Na_2O_2 -fusion step.

¹F. E. Beamish and J. J. Russel. "The Assay of Platinum Metals." *Industrial and Engineering Chemistry* 8:2. March 15, 1936.

ELECTROLYSIS

REMOVAL OF PLUTONIUM FROM SOIL

Jack L. Long, John A. Hayden,
and Terry F. Rees***

Summary

The feasibility of electrolytically removing plutonium and uranium from contaminated soil was demonstrated. Electrolysis was essential to the formation of a foam fraction which concentrated the radioactivity from the balance of the electrolyte. The foaming agents were attributed to yucca root constituents that were indigenous to the soil samples tested.

Experimental

Soil samples, of from 10 to 20 grams each, containing varying trace amounts of radioactive constituents, were electrolyzed in aqueous solutions adjusted to a pH of 11.5 at a potential of 13 volts and a current of approximately 0.3 amperes. The soil was suspended in the alkaline solution by physical agitation during the electrolysis experiments. A large portion of the radioactivity was found to collect in a foam fraction. The electrolysis appeared essential for foam formation, since the foam was not formed by simply bubbling air through the mixture nor when soil, which had been washed and wet-seived, was electrolyzed. Addition of pulverized yucca plant roots to this washed and wet-seived soil restored the foaming on electrolysis. Apparently, washing and seiving had removed the foaming agent from the soil.

The cause of the foaming observed during these soil electrolysis experiments was attributed to yucca root constituents, saponins and sapogenin hydrolysis products. The principle yucca component separated by water extractions and organic-solvent extractions was characterized as a plant starch cellulosic (amylose). This starch component probably did not contribute to the

foaming, but it did form a colloidal gel when the yucca root was pulverized and extracted with distilled water. Silicates and carbonates were always present in the water, in the organic solvent extracts of the roots, and in the soil. These silicates and carbonates probably provided an alkaline medium which either was necessary for or enhanced the foam formation.

ELECTRON MICROSCOPY

CHEMICAL SURFACE ANALYSIS USING ELEMENTAL X-RAY MAPPING

GeorgiAnne K. Fukuhara

Summary

Elemental X-ray mapping, in conjunction with energy dispersive X-ray analysis, can be used to relate the chemical structures with surface topographies of various samples. Using a scanning electron microscope-energy dispersive system (SEM-EDS), the depth of penetration of a catalyst impinged on an Inconel® filter frit surface was determined. Elemental X-ray mapping provided an easy and definitive method of locating the catalyst lodged in the pores of a cross section of the frit. In another application of SEM-EDS, plutonium (Pu) was mapped to determine its location on the surface of a metallic fragment.

Experimental

The equipment used to obtain the elemental X-ray mappings includes a Cambridge S-4 Stereoscan Microscope, a Kevex lithium-drifted silicon [Si(Li)] detector, a Kevex Model 4941 image enhancer, and a Tracor Northern 880 analyzer with PDP11 computer. The detector has an energy resolution of 160 electron volts which is the full width at half the maximum peak height for the K α line for a manganese standard.

Figure 1 is a micrograph of a section of an Inconel® filter frit that was subjected to a stream of catalyst from outside the ring. The flow is indicated by the

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FIGURE 1. Section of Inconel® Filter Frit

FIGURE 2. Cross Section of the Inconel® Filter Frit Impregnated With Catalyst. Magnification 188X.

arrow. A section of the ring was cut and mounted so that the cross-sectional face was exposed and acid-etched. Figure 2 depicts the outside edge at the bottom of the micrograph (indicated by arrows) and the inside of the ring toward the top. The metal is shown as the light areas, and the pore spacings are the black areas. The catalyst appears as particles lodged in the pore spacings toward the outside edge.

Qualitative X-ray data indicates that Inconel consists largely of nickel (Ni), chromium (Cr), and iron

(Fe). Both the Inconel and the mounting material are practically devoid of any aluminum (Al). The catalyst is chromium oxide and sodium carbonate in an alumina base. An X-ray map for the Al $K\alpha$ line, acquired at an accelerating voltage of 20 kilovolts (kV) with the image enhancer set at 5, is shown as Figure 3. The X-ray photons appear as white dots, which correspond with Al in the catalyst. Thus, elemental X-ray mapping provides a means of locating the catalyst lodged on the pores of a cross-section of the frit and the depth-of-penetration of the catalyst subsequently can be determined.

FIGURE 3. X-Ray Mapping of Catalyst-Impregnated Filter Frit for Aluminum. Magnification 188X.

FIGURE 4. Section of Metallic Fragment. Alpha activity is concentrated in areas indicated by arrows. Magnification 775X.

FIGURE 5. X-Ray Mapping for Plutonium of the Section of Metallic Fragment in Figure 4. Magnification 775X.

FIGURE 6. Section of Metallic Fragment. Arrows indicate areas of contamination. Magnification 775X.

In a separate application, Pu was mapped to determine its location on the surface of a metallic fragment. Figures 4, 6, and 8 show sections of the

metallic fragment, which had a small amount of alpha activity localized on one side only. To determine the nature of the contamination, an

FIGURE 7. X-Ray Mapping for Plutonium of the Section of Metallic Fragment in Figure 6. Magnification 775X.

FIGURE 8. Section of Metallic Fragment. Contaminated regions are indicated as areas a and b. Magnification 780X.

FIGURE 9. X-Ray Mapping for Plutonium of Area a in Figure 8. Magnification 3800X.

FIGURE 10. X-Ray Mapping for Plutonium of Area b in Figure 8. Magnification 3800X.

X-ray map for the Pu M line was acquired at an accelerating voltage of 20 kV and an enhancement factor of 5. Figures 5, 7, 9, and 10 are the respective X-ray mappings for Figures 4, 6, and 8. The plutonium is displayed as concentrations of white dots, which correspond with the areas pointed out by

the arrows in Figure 4, 6, and 8. Thus, the contamination appears to be discrete and concentrated rather than dispersed and homogenous.

Elemental X-ray mapping provides unique information about the chemical makeup of a surface

structure. The mappings, however, will contain some extraneous X-ray (white) dots that may be due to scattering in the background and not necessarily due to characteristic X-rays. Therefore, with this particular system, the method is qualitative to some extent. This background effect can be reduced at higher magnifications and over a smaller scan area.

GALLIUM IN PLUTONIUM METAL

Harvey L. Bramlet

Summary

Gallium (Ga) can be determined on metallurgically-prepared plutonium (Pu) samples using the X-ray wavelength spectrometer on the scanning electron microscope (SEM). The method is designed as a research aid to investigate differences in Ga concentrations within inhomogeneous alloys.

Experimental

Samples of Pu-Ga alloys are mounted in epoxy cylinders, 1¼ inch in diameter by ½ inch thick and polished by conventional metallurgical techniques. After polishing, the mount is cleaned with solvent to remove all particulates, then painted with silver paint except for a small area of the metal surface. The mount is placed in the SEM, the sample chamber is evacuated, and the surface of the sample is examined for a spot suitable for analysis. Once the desired spot is found, the X-ray spectrometer is used to measure peak intensity and background on both sides of the gallium K α line. The two backgrounds are averaged, and the net intensity above background is calculated.

The above process is repeated in its entirety on a small block of gallium arsenide standard which may remain in the SEM. The intensity of the sample is divided by the intensity obtained from the gallium arsenide to give a *K-ratio*. All of the calculations to this point are performed on a programmable calculator. A Tracor 880® is used to perform a quantitative matrix correction, converting X-ray intensities to concentrations.² The

instruments and operating parameters are listed below.

Equipment

- a. Cambridge S-4® scanning electron microscopy fitted with metallurgical stage and Microspec spectrometer.
- b. Ortec® nucleonics consisting of amplifier; single channel analyzer (Model 490A), counter, and timer (Model 776); and high voltage power supply (Model 456).
- c. Keithley Instruments® 410A picoammeter (for specimen current).
- d. Tracor 880® X-ray analysis system (based on a PDP-11 computer with 24K core).
- e. Decwriter® II.

Operating Parameters

- a. Microscopy accelerating voltage: 20 kV.
- b. Microscope resolution: ~200 Angstroms.
- c. X-ray resolution: ~1 micrometer.
- d. Working Distance: Calibration of microscope to 13 millimeters working distance.
- e. Magnification: Not less than a factor of 500X.
- f. Specimen current: $\sim 1 \times 10^{-7}$ ampere.
- g. X-ray take-off angle: 45°.
- h. X-ray spectrometer:
 1. Slit - 1.1 millimeters
 2. Crystal - LiF
 3. Ga K α angle - 1.3395 LiF Angstrom equivalents
 4. Background One - 1.3895 LiF Angstrom equivalents
 5. Background Two - 1.2895 LiF Angstrom equivalents
 6. Count Rate on GaAs - 10,000 counts per second

² Joe H. Doyle. Internal Communication. Rocky Flats Plant. May 1979.

The method is designed to study differences of gallium concentrations within a sample as a research aid. Due to inhomogeneities within alloys, it is sometimes difficult to get a sample average. SEM operating conditions are critical in obtaining satisfactory results. The lower detection limit is about 0.1 weight percent; therefore, the method is suitable for the common range of Ga concentrations in Pu-Ga alloys. The standard deviation is about 0.015 weight percent at Ga concentrations of 1.0 weight percent.

ANALYSIS OF PLUTONIUM METAL DEFECTS USING SCANNING ELECTRON MICROSCOPY

John K. Fraser

Summary

Metal defects are located by radiographic analysis using nondestructive X-ray techniques on plutonium (Pu) parts. Samples of metal including the defect areas are made using the Cambridge S-4® scanning electron microscope (SEM), and carbon analysis is accomplished with the Microspec spectrometer.

Experimental

The initial sample preparation is performed by the Metallography Laboratory. The metal sample is mounted in a plastic mount approximately 2.5 centimeters in diameter. Surface defects can be analyzed as received, but internal defects are located by grinding the metal surface and periodically examining the surface by optical microscopy. The equipment used in these analyses includes: a Cambridge Stereoscan S-4® scanning electron microscope fitted with a Microspec wavelength dispersive X-ray spectrometer and a Kevex® lithium-drifted silicon [Si(Li)] detector; an Ortec® 456 high voltage power supply, 490A amplifier and single channel analyzer, 776 counter, and 449 rate meter; a Keithley® 410A picoammeter, a Tracor Northern 880® data analysis system with

a Digital Equipment Corporation® PDP11 computer, a Digital Decwriter® II printer, and a Denton® DV-502 vacuum evaporator.

The sample prepared by the Metallography Laboratory is mounted on an aluminum sample holder and cemented into place using silver-conducting paint. All surfaces of the sample, except the area immediately around the defect, are painted to provide a conducting surface and to seal off contamination. Lead tape is placed around the defect to form a window to reduce the radiation from Pu which causes interference in the analysis.

Energy dispersive X-ray (EDX) analysis is made on numerous locations in and around the defect to locate elevated concentrations of any specific elements. An accelerating potential of 20 kilovolts (kV) is used, and the data are analyzed by the Tracor Northern 880® analyzer. All elements with atomic number equal to and greater than sodium are detected simultaneously by this method.

Each defect is analyzed for carbon using the Microspec Spectrometer attachment to the SEM. A small piece of graphite is mounted on the sample near the defect, and the ratio between the standard- and defect-area count rates is reported. For carbon, a diffracting crystal of lead stearate and an open-slit setting are used. The peak position is 1.782 angstroms (Å) equivalent LiF wavelength (EQL), and backgrounds are taken at about 1.4 and 2.1 Å EQL. The diffracted X-rays are detected by an argon-flow proportional counter having the following settings: counter voltage, 1500 volts (V); amplifier gain, 0.6 coarse, 32 fine; baseline, 0.5 V; and window, 4 V. The stage sample carriage is rotated 90° counterclockwise from its position for EDX counting and tilted to the 45° position. An accelerating potential of 20 kV and an 11-millimeter working distance are used on these samples. The specimen current between the sample and standard is kept constant by adjusting condensers and monitoring with a picoammeter.

The defect samples are then placed in a vacuum evaporator, where a thin layer of gold or carbon is vaporized on the sample surface. Polaroid® 55 P/N film is used to take photomicrographs of the entire defect and selected areas of interest. A

FIGURE 11. Sample W01024-1A. Arrows indicate high concentrations of carbon. Magnification 100X.

FIGURE 12. Sample W01024-3B. Defect area containing no significant concentrations of impurity elements. Magnification 100X.

FIGURE 13. Sample W01024-5C. Defect area at a magnification of 20X. The area indicated by arrows is shown at a greater magnification in Figure 4.

FIGURE 14. Sample W01024-5C. High-concentrations of carbon were detected in slightly darker areas along edge of defect. Magnification 200X.

typical defect at 100X magnification is depicted in Figure 11. Carbon concentrations from about 4 to 12 times background were detected in the locations indicated by arrows. Figure 12 shows, at 100X magnification, a micrograph of a defect in which no significant concentrations of any

element except Pu were detected. Figure 13 is a micrograph of a defect at 20X magnification, and Figure 14 is a 200X magnification of the area between the arrows on Figure 13. The slightly darker areas along the side of the defect in Figure 14 have carbon concentrations from

4 to 6 times background. Carbon concentration in the defect itself was approximately background level.

Investigating the elemental data and the appearance of defects helps the metallurgist learn more about the causes of the defects and how to eliminate them. Voids without elemental composition appearing in metal may be formed by too rapid cooling following pouring into molds. Tantalum impurities probably come from the mold and calcium from the mold coating. Carbon may originate from graphite molds. Phosphorous and chlorine may be deposited during cleaning at some stage in the process. Silicon, iron, and other elements may be impurities in the metal itself.

EMISSION SPECTROSCOPY

CARRIER-DISTILLATION METHOD FOR IRIDIUM AND YTTRIUM IN PLUTONIUM DIOXIDE

Ronald D. Thiel

Summary

The emission spectrographic determination of iridium (Ir) and yttrium (Y) in plutonium dioxide (PuO_2) has been developed by using a carrier-distillation method. This procedure requires minimal sample preparation and incorporates a Stallwood jet to provide an oxygen atmosphere for the direct current (D.C.) arc plasma. Detection limits are 25 micrograms per gram ($\mu\text{g/g}$) for Ir and 600 $\mu\text{g/g}$ for Y.

Experimental

To analyze Ir and Y in PuO_2 , it is advantageous to keep the sample in the solid form. Dissolving the sample for an atomic absorption spectroscopy procedure would involve two separate fusions, thus creating extensive sample preparation. This method results in many additional steps in the analytical procedure, thus greatly increasing the possibility of

TABLE 1. Spectrographic Parameters for Ir and Y Determinations

Parameter	Setting/Description
amperage:	4 amperes (short circuit)
exposure time:	65 seconds
electrode gap:	4 millimeters (centered about optical axis)
counter electrode:	UCP type 1346B
sample electrode:	UCP type 100-L
entrance slit:	2 millimeters in height, 10 micrometers in width
photographic plate:	Eastman type SA-1
wavelength range:	2900 to 3500 Angstroms ($\text{\AA}$)
analytical wavelengths:	Ir = 3220.78 $\text{\AA}$ Y = 3242.28 $\text{\AA}$ Co = 3044.00 $\text{\AA}$
atmosphere:	Oxygen = 4.2 liters per minute flow rate

errors. Samples in the solid state can be analyzed by emission spectroscopy with relatively little sample preparation. Emission spectroscopy is, therefore, the method of choice for this analysis.

In the emission spectroscopy procedure, PuO_2 samples are ignited for 30 minutes in an 800 °C muffle furnace to insure total oxide formation and sample homogeneity. The samples are then mixed with finely-ground silver chloride (AgCl) and powdered cobalt oxide (CoO). This procedure produces a matrix consisting of a AgCl concentration of 15 weight percent and a Co concentration of 200 $\mu\text{g/g}$. Three 120-milligram charges are loose-loaded into graphite electrodes. The samples are then analyzed spectrographically in the D.C. arc mode in accordance with the parameters listed in Table 1. The detection limits are 25 $\mu\text{g/g}$ for Ir and 600 $\mu\text{g/g}$ for Y.

The addition of AgCl to the sample to function as a carrier was originally investigated by Scribner and Mullin.³ The incorporation into the powdered sample of a small quantity of a substance of inter-

³ Bourdon F. Scribner and Harold R. Mullin. "Carrier-Distillation Method for Spectrographic Analysis and Its Application to the Analysis of Uranium-Base Materials." *Journal of Research of the National Bureau of Standards* 37:379. December 1946.

FIGURE 15. Emission Spectroscopy Calibration Plot of Iridium-Cobalt (Internal Standard) Absorbance Ratio as a Function of Iridium Concentration

mediate boiling point, such as AgCl, facilitates the distillation of the volatile impurities. The carrier sweeps the volatile impurities out of the refractory PuO₂ matrix, moderates the arc discharge character, and adds to the positive electricity flow. As a result, the background due to the plutonium spectrum is held to a minimum. Yttrium oxide (Y₂O₃), which has a boiling point of 4300 °C, is much more refractory than iridium oxide (IrO₂). Therefore, it is less sensitive in this analytical procedure.

A Stallwood jet is used to provide an oxygen atmosphere for the D.C. arc plasma. At the Los Alamos Scientific Laboratory, an oxygen atmosphere, in conjunction with the carrier distillation method, is applied in the determination of other refractory elements.⁴ The oxygen atmosphere has the effect of minimizing background, thus allowing a longer arc time, which results in a relatively clean spectrum.

A set of standard PuO₂ samples with Ir and Y at concentrations ranging from 10 to 1000 µg/g was prepared by converting Pu metal to PuO₂. The metal was dissolved, converted into the oxalate, and ignited to the oxide according to a Rocky Flats Procedure.⁵ Upon dissolution, the samples were spiked with aliquots of hydrochloric acid solution containing 1000 µg/g each of Ir and Y. Each standard also was spiked with 400 µg/g Co, which serves as an internal standard.

Quantitative densitometer readings were made on the Ir lines at 3220.78 Angstroms in the 100 to 1000 µg/g range with the use of a 10 percent/100 percent filter. Four standards were analyzed to produce the calibration plot shown in Figure 15. This plot was particularly linear in the 100 to 400 µg/g region, as indicated by a linear least-squares fit of $y = 0.0093 \times -0.023$ and a correlation coefficient of 0.999. Replicate analyses of each of the Ir standards were completed to obtain

⁴ James E. Rein et al., editors. "Determination of Metal Impurities by Emission Spectroscopy Using the Carrier-Distillation Technique." *Methods of Chemical Analysis for FBR Uranium-Plutonium Oxide Fuel and Source Materials*. LA-4622. Los Alamos Scientific Laboratory of the University of California, Los Alamos, New Mexico 87545. February 1971. Page 105.

⁵ John D. Grooms. Private Communication. Rocky Flats Plant. January 1979.

a statistical evaluation for method precision. Over the Ir concentration range of 100 to 600 µg/g, the relative standard deviations from the means varied from 5.0 to 15.9 percent.

Because of background interferences and poor sensitivity for the Y line at 3242.28 Angstroms, it was not feasible to obtain accurate densitometer readings. Consequently, the Y determinations were accomplished by visual comparison with standard plates, and no statistical treatment of data was attempted.

GAS CHROMATOGRAPHY

POLYCHLORINATED BIPHENYLS IN TRANSFORMER OIL

Karl N. Kirchner

Summary

A simple method has been developed to determine polychlorinated biphenyls (PCB's) in transformer oils by direct injection into the gas chromatograph. The lower limit of detection was established at 10 milligrams per liter.

Experimental

Pyranol,® a PCB, was used as a dielectric in transformers at Rocky Flats until it was recently replaced with a mineral oil dielectric. A gas chromatographic method, in which the samples are injected directly into the chromatograph, was developed to monitor the residual PCB in the mineral oil. Previous PCB analysis methods involved solvent extraction and preconcentration steps prior to analysis; consequently, the current method represents a considerable time savings.

Sample and standards are diluted 1 to 5 in hexane and introduced into a Varian model 2400 gas chromatograph, equipped with a scandium tritide electron-capture detector and operating with an

oven temperature setting of 200 °C. A 6-foot glass column is packed with a commercially-prepared packing for pesticide residues, consisting of 1.5 percent SP-2250® ± 1.95 percent SP-2401® on 100/120 mesh Sepelcoport®. Standards of Aroclor® 1260 are prepared in the concentration range of 10 to 80 milligrams per liter (mg/l) of Aroclor-free mineral oil. The minimum detection limit for a 3 microliter aliquot is 10 mg/l.

IMPROVED METHOD FOR TRACE ENRICHMENT OF POLYCHLORINATED BIPHENYLS IN WATER

Kathleen G. Cummings and Richard D. Lally

Summary

An alternative method for preconcentrating polychlorinated biphenyls (PCB's) was tested and found to be superior to the previously used solvent-extraction method. Using Waters Associates C₁₈ packing, PCB's were concentrated and subsequently eluted with hexane. Recoveries of 87 percent or better were achieved while relative standard deviations were less than 1 percent.

Experimental

Tolerance limits for PCB discharges have been proposed at 0.001 microgram per liter (ppb) level on a daily average.⁶ Therefore, to implement analytical monitoring, it is necessary to develop suitable techniques for the concentration of these pollutants. Favorable results have been reported using a macromolecular resin such as Amberlite® XAD-2.⁷ Recoveries for this sorbent ranged from 78 to 86 percent. The application of Tenax®, a

porous polymeric material, has also been investigated.⁸ However, mineral oils at the levels typically found in waste effluents, deactivate Tenax, resulting in low recoveries of micropollutants. Also, both these methods require a relatively large volume of resin [5 to 6 cubic centimeters (cm³)]; therefore, large volumes of solvent are necessary for elution. The column eluate must be dried and evaporated in order to concentrate trace organics.

The method previously used at the Rocky Flats Plant for concentrating PCB's involved partitioning water samples with a mixture of 15 volume percent (%) methylene chloride and 85% hexane. The organic layer was then evaporated to rid the mixture of methylene chloride and to further concentrate the PCB's. Typical recoveries for this solvent-extraction procedure are given in Table 2. The apparatus used for the gas chromatographic determinations was a Varian® Series 2400 Gas Chromatograph equipped with a tritium-electron capture detector and a silanized glass column packed with 1.5% SP-2250® + 1.95% SP-2401® on 100/120 mesh Supelocoport® AW-DMCS. The oven temperature was maintained at 200 °C, the injection port at 222 °C, and the detector at 246 °C. Recoveries at the 95% confidence interval averaged 65 ± 2%, 66.7 ± 2.1%, and 86.7 ± 2.1% for 2,4,2',4'-tetrachlorobiphenyl, Aroclor® 1248, and p,p'-dichlorodiphenyl-dichloroethylene (DDE), respectively.

The present method involves passing a known volume of water directly through a 1-cm³ column containing Waters Associates Bondapak C₁₈/Corasil packing (Sep-Pak®). A vacuum filtration apparatus is set up so that the Sep-Pak cartridge fits into a rubber stopper placed in the top of a 1000-milliliter (ml) filter flask. The top of the Sep-Pak is connected with Tygon® tubing to the end of a 1000-ml separatory funnel supported on a ring stand. Sample water is placed in the separatory funnel and allowed to filter through the Sep-Pak. PCB's retained on the nonpolar packing material are eluted from the cartridge with 1 ml hexane. Recovery data for this method are also summarized

⁶ Chapter I—Environmental Protection Agency, Part 129—Toxic Pollutant Effluent Standards, "Standards for Polychlorinated Biphenyls (PCBs)." *Federal Register*, Volume 42, Number 22. Wednesday, February 2, 1977.

⁷ J. A. Coburn, I. A. Valdmanis, and A. S. Y. Chau. "Evaluation of XAD-2 for Multiresidue Extraction of Organochlorine Pesticides and Polychlorinated Biphenyls from Natural Waters." *Journal of the Association of Official Analytical Chemists* 60:224. 1977.

⁸ V. Leoni, G. Puccetti, R. J. Colombo, and A. M. D'Ovidio. "The Use of Tenax for the Extraction of Pesticides and Polychlorinated Biphenyls from Water." *Journal of Chromatography* 125:399. September 1976.

TABLE 2. Recovery Data for Gas Chromatographic Determination of Polychlorinated Biphenyls (PCB's) in Water Samples

PCB Type	Contamination Range (micrograms per liter)	Mean Recoveries From Triplicate Determinations ^a		
		Solvent Extraction ^b (Prior Method)	Sep-Pak® (New Method)	Trace Enrichment (Oil Contamination) ^c
2,4,2',4'-tetrachlorobiphenyl	1.24 to 3.06	65.0 ± 4.0%	88.0 ± 2.0%	87.3 ± 3.1%
Aroclor® 1248	1.16 to 3.86	66.7 ± 4.2%	90.7 ± 1.2%	89.7 ± 4.2%
p,p'-dichlorodiphenyl-dichloroethylene	1.28 to 3.46	86.7 ± 4.2%	100.0 ± 0.0%	99.0 ± 2.0%

a. Recoveries are calculated from peak-area ratios determined by gas chromatography conditions described in test. The ± results are the 95 percent confidence intervals (±2 mean standard deviations).

b. Each sample was partitioned three times with 60 milliliter portions of 15 volume percent (%) methylene chloride and 85% hexane and evaporated to a final sample volume of 3 milliliters.

c. The water samples were deliberately contaminated with 1 part per million mineral oil to determine if any deactivating effects on the Sep-Pak (Waters Associates Bondapak C₁₈/Corasil packing) would occur.

in Table 2. The average recoveries were $88 \pm 1\%$ for 2,4,2',4'-tetrachlorobiphenyl, $91 \pm 6\%$ for Aroclor 1248, and quantitative for the internal standard, p,p'-DDE.

To determine the effect of oil on the recoveries, water samples were artificially contaminated with 1 part-per-million mineral oil as well as *spiked* with known amounts of PCB's. Data are given in Table 2. It is evident that the C₁₈ packing is not significantly deactivated by small quantities of oil typical of those concentrations found in industrial effluents (i.e., from 0.3 to 0.7 milligram per liter).

Compared to the solvent extraction method, the major advantages of the Sep-Pak enrichment method are the considerable amount of time saved, the possible automation of the process, and the presence of fewer interfering substances in the column eluate. Since the method facilitates on-site sampling, loss of trace contaminants by absorption on the walls of storage containers can be avoided. Such a small volume of packing is needed that cross contamination of samples can be eliminated by dedicating one Sep-Pak to each sample and then discarding it. Also, more selective control exists over the elution of interferences than with solvent extraction. With the proper choice of solvents, interfering substances can be eluted separately from the PCB's. Since no evaporation step is necessary and little glassware is used, there is less chance for sample contamination and loss of sample. The handling of toxic PCB's is

minimized. Finally, in comparison to other sorbent methods, specifically those using Tenax and Amberlite XAD-2, the PCB's are eluted in only 1 ml of solvent instead of 75 ml or more. Therefore, smaller quantities of expensive pesticide-grade solvent are utilized, and the problems inherent in evaporating excess solvent are eliminated.

LIQUID CHROMATOGRAPHY

CHLORPHENOXY ACID HERBICIDES IN WATER BY REVERSE-PHASE LIQUID CHROMATOGRAPHY

Kathleen G. Cummings

Summary

The chlorphenoxy acid herbicides, 2,4-dichlorophenoxyacetic acid (2,4-D) and 2-(2,4,5-trichlorophenoxy) propionic acid (2,4,5-TP) (silvex), have been assigned maximum contaminant levels (mcl's) of 0.1 milligram per liter (mg/l) and 0.01 mg/l, respectively by the Environmental Protection Agency (EPA). These two herbicides are available in different chemical forms (free acids, butyl esters, and amine salts). Using reverse-phase liquid chromatography, the different chemical forms of 2,4-D and silvex can be detected at levels well below the EPA-specified mcl's.

Experimental

To perform an assay of 2,4-D and silvex by gas chromatography (GC), the various chemical forms must first be converted to a single volatile derivative (e.g., the methyl ester). By this method, derivatization, clean up, and analysis requires five hours. In addition, it is impossible to distinguish between the various chemical forms and to determine their separate concentrations. On the other hand, the liquid chromatography (LC) method enables a simultaneous assay of the separate forms of the chlorphenoxy acid herbicides and takes less than one hour to complete.

The LC method employs a Waters Associates Model 6000A solvent delivery pump equipped with a Model 440 absorbance detector and a 30 centimeter μ -Bondapak C₁₈ column. To achieve a gradient system, a Fluid Metering Inc. Model RP laboratory pump has been set up to deliver a second solvent into the primary solvent reservoir at a constant rate.

Prior to analysis, a preconcentration step was performed using 1 cubic centimeter (cm³) of Waters Associates μ -Bondapak C₁₈/Corasil® packing (Sep-Pak®). It was necessary to acidify the sample water with 1 percent by volume acetic acid to convert acid salts to the carboxylic acid form and improve recovery from the Sep-Pak. By passing 1 liter (1) of sample water through a Sep-Pak and eluting the retained herbicides with 1 milliliter (ml) methanol, recoveries averaged 88 percent (%) for 2,4-D acid, 86% for silvex, and 80% for 2,4-D butyl ester. With some samples, it was necessary to clean up interfering organics by eluting them from the Sep-Pak with approximately 2 ml of a mixture of 50% methanol and 50% water. This procedure did not significantly decrease recoveries.

An 18-minute separation of 2,4-D acid, silvex, and 2,4-D butyl ester, eluting in that order, was achieved using a solvent gradient of 50% to approximately 90% methanol in water. The mobile phase was made 1% by volume in acetic acid. The flow rate was kept at 1.7 ml per minute as methanol (1% in acetic acid) was pumped into the primary solvent reservoir at a constant rate determined by the initial volume of solvent. The detection limit for the herbicides at 280 nanometers and 0.005 absorbance

units full scale allowed determinations as low as 0.1 microgram per liter (μ g/l or ppb). While the gradient used was not highly reproducible, at isocratic operation detection limits were severely decreased because of peak broadening.

In addition, an isocratic determination of 2,4-D acid and bromacil (5-bromo-3-sec-butyl-6-methyluracil), also covered by EPA regulations, was carried out on the potable water supply at the Rocky Flats Plant. Trace herbicides were preconcentrated from 1 liter of water onto a Sep-Pak as before. Recoveries from the nonpolar packing, using 1 ml methanol for elution, averaged 78% for bromacil. Elution of the herbicides was completed in six minutes, with 2,4-D acid being retained more strongly than bromacil. The mobile phase was 50% methanol and 50% water made 1% by volume in acetic acid, and the flow rate was 1.7 ml per minute. The detection limit for bromacil was also 0.1 μ g/l.

MASS SPECTROSCOPY

SOLUTION ANALYSIS BY SPARK SOURCE MASS SPECTROMETRY

Clyde E. Michel

Summary

A technique enabling solution to be conveniently analyzed by Spark Source Mass Spectrometry (SSMS) is described. Small volumes of a sample, typically 10 microliters, are dried on the tips of graphite electrodes. The electrodes are sparked, and the elemental information is recorded in the normal manner using the photoplate detector.

Experimental

Solids are actually the only phase that can be directly analyzed by SSMS. Conducting materials such as metals may be analyzed directly; however, nonconducting solid materials generally must be mixed with a suitable conducting material such as graphite or silver powder and pressed into electrodes

prior to analysis. Solutions must be evaporated to dryness, and any residue is then mixed with a conducting material before it is analyzed.

A previously-developed technique has been adapted at Rocky Flats for solutions, eliminating the sample preparation steps of evaporation to dryness, mixing, and pressing into an electrode configuration. Instead, a small amount of the sample solution is dried directly on the tips of high-purity graphite electrodes. The electrodes are then sparked, and an analysis of material on the electrode tips is performed.

In this method, about 10 microliters (μl) of an aqueous sample containing an internal standard element are added to the flat tip of a high-purity graphite electrode, and the drop of solution is dried onto the tip using a heat lamp. Two electrodes are prepared and are then analyzed in the usual manner, except that the internal standard and the element of interest must be compared on the same photoplate exposure because of the depletion of the sample material during sparking. Also, when gradual exposures are obtained, line densities must be measured by a densitometer instead of the visual comparison method. Erbium is often used for the internal standard because it is absent in most samples and possesses several isotopes having a wide range of abundance applicable over a large exposure range.

As little as 1 microgram of the element of interest in one milliliter of sample solution can usually be analyzed. With about 10 μl of the sample solution added to each electrode, only about 20 nanograms of an element need be present to be measured quantitatively. For many types of aqueous samples, as well as for small amounts of solid samples that can be readily dissolved, this method is more rapid and convenient than conventional SSMS techniques. It also has the advantage of insuring sample homogeneity. As with other SSMS analyses, all elements with atomic weights greater than lithium may be determined in a single sample aliquot.

With careful calibration, accuracies of about ± 30 relative percent for most elements are obtained. The technique has been used to determine trace impurities in plutonium solutions, environmental samples, and high-purity water samples and has the

potential to be applied to a wide variety of liquid samples.

SAMPLING METHODS

PORTABLE GAS-SAMPLING SYSTEM

*Duane I. Hunter, Merle L. Ralston,
and Orville F. Lee*

A portable system has been designed and fabricated to sample headspace gas in shipping containers in remote locations for subsequent tritium analysis. The tritium analysis involves evacuating a septum-fitted liquid scintillation-counting vial, puncturing the container to be sampled, and expanding headspace gas to a pressure of 200 torr into the vial through a vacuum manifold. Liquid scintillation cocktail is introduced into the vial using a hypodermic needle. The sample is then taken to the main laboratory area where the scintillation counting, calculating, and reporting are performed.

Previously, sampling in an area outside the laboratory was a problem because, for proper sampling, a large amount of equipment was required. This equipment included a pump, a vacuum manifold, a pressure-measuring device, and other laboratory supplies.

The portable gas-sampling system consists of a cart, similar to a tool caddy, having four drawers for storage of vials, septa, tools, lead aprons, and surgeons' gloves. The cart is equipped with a Sargent-Welch 1400 fore pump, a small vacuum manifold, and a Bell and Howell 1000 pressure transducer with electronic readout for pressure measurements.

The new system allows the operator to have the equipment assembled for sampling on short notice and eliminates the problems of moving various pieces of equipment for remote sampling. Use of the remote sampling station is not limited to tritium analysis, but may be used to sample atmospheres from any other operation in which a portable vacuum system is advantageous.

THERMAL ANALYSIS

EVALUATION OF FLAMMABILITY HAZARDS OF HEPA-FILTER CONSTRUCTION MATERIALS

*Patricia A. Hyman, Duane I. Hunter,
and Merle R. Ralston*

Summary

To adequately assess the flammability hazards of materials used in HEPA filters, a special flameless ignition-testing apparatus has been developed. The apparatus duplicates, on a miniature scale, the heated plenum used in HEPA-filter testing at the National Test Center. Materials to be evaluated are made into a miniature HEPA filter which is inserted into the miniature plenum with heated airflow. Evaluation of the materials is accomplished by a combination of visual observations and recorded temperature differences between the heated air and the filter materials.

Experimental

Concern over the ability to predict the flammability hazards of HEPA-filter components arose when a filter consisting of Flander's Y-100 fiberglass media and a polyvinyl chloride/polyvinyl acetate (PVC-PVAc) copolymer-coated aluminum separator caught fire and burned during a heated-plenum test at the National Test Center. According to analytical results, large amounts of trapped tetrahydrofuran (THF) solvent were evolved as the PVC-PVAc copolymer coating softened. At the elevated temperature of the test (399 °C), apparently sufficient concentration of THF solvent vapors existed in the filter to ignite and burn the filter, melting the aluminum separator material. (The autoignition temperature of THF is 321 °C.) The cost of constructing full-size HEPA filters and of performing the heated-plenum test is considerable; therefore, it is desirable to determine flammability hazards before constructing a filter for testing.

Efforts to assess flammability hazards of various materials using mass spectrometry outgas and thermogravimetric analysis (TGA) methods proved ineffective because only the decomposition temperature of polymeric materials and the nature of the

decomposition products could be determined. Since the decomposition products were flammable, there was no method for determining the minimum concentration necessary in a HEPA filter for autoignition.

The actual test conditions employed at the National Test Center had to be duplicated as accurately as possible to predict the flammability of a full-size HEPA filter composed of the test materials. This was accomplished by constructing a miniature plenum and miniature HEPA filters. Figure 16 illustrates the construction of the miniature filter, which is a scaled-down version of a full-size filter measuring 24 × 24 × 11½ inches. The miniature filter measures 2 × 2 × 2 inches and consists of a continuous sheet of fiberglass media (2 inches wide) woven around rigid, pleated separator sheets measuring 2 × 2 inches. The miniature filter provides approximately 52 square inches of media surface area compared to 200 square feet in a full-size filter.

The miniature heated plenum (or flameless ignition-testing apparatus) is shown schematically in Figure 17. The *plenum* is a 12-inch length of square Pyrex glass tubing with internal dimensions of 2 × 2 inches. The glass allows visibility of the filter during the test and can withstand temperatures as high as 600 °C. Laminar airflow is achieved by packing the interior of the Pyrex tube with 1½-inch long, ¼-inch outside diameter quartz tubes. Heated airflow is provided by a Sylvania GTE Flameless Electric Burner connected to the plant air system. Airflow is measured using a rotameter and is regulated to deliver an equivalent of 1000 standard cubic feet per minute (scfm) per 200 square feet of media (or 1.8 scfm per 52 square inches of media). Heat loss through the Pyrex glass is avoided by wrapping three-quarters of the tube with heater tape heated to 400 °C. Temperature measurement is accomplished using two chromel-alumel thermocouples, each attached to a Doric Trendicator® 400A digital readout calibrated in degrees Celsius (°C). A photograph of the system being loaded with a miniature filter for testing is shown in Figure 18.

During a flameless ignition test, one thermocouple is placed directly in front of the sample filter and the other is inserted inside the filter. Thus, measure-

FIGURES 16(a) and (b). HEPA - Filter Design

FIGURE 17. Flameless Ignition Apparatus

FIGURE 18. Filter Media for Testing is Being Loaded Into the Flameless Ignition Apparatus

ments of the temperature differential that can develop between the heated air stream and the filter materials are possible. A rapid, large increase in temperature is indicative of combustion. Small temperature differentials on the order of 10 to 30 °C may be caused by differences in heat capacity and thermal conductivity between the air, the filter materials, and thermocouples of different masses with no actual combustion occurring.

The apparatus enabled duplication of the National Test Center's results for the filter composed of Flander's Y-100 media and aluminum separators coated with PVC-PVAc. At approximately 400 °C air temperature, the filter material ignited and burned with a red glow. The filter components were examined following the test, and the PVC-PVAc coating was observed to have had discolored and peeled off the aluminum. Furthermore, much of the aluminum separator material had melted, and the media was brittle and crumbling.

The same apparatus was then used to test a filter composed of Flander's Y-100 media and epoxy resin-coated aluminum separators from the Aluminum Filter Company. No visible evidence of combustion was observed during the test and the temperature

differential never exceeded 20 °C. Examination of the filter components following the test revealed that although the epoxy coating was badly discolored, it remained adhered to the aluminum surface and the media was only slightly discolored and still flexible.

The apparatus should prove to be a useful tool for evaluating prototype HEPA filter materials to be tested at the National Test Center without the need of constructing expensive full-size test filters and without risking potential fire hazards during the testing.

IDENTIFICATION OF NOMEX® AND KAPTON® IN FIBERGLASS HEPA-FILTER MEDIA

Patricia A. Hyman and Duane I. Hunter

Summary

Routine analytical methods used to identify organic additives in fiberglass filter media yield ambiguous and misleading results when the organic additive is Nomex® (an aramid fiber manufactured by DuPont).

To obtain a positive identification and to distinguish Nomex from Kapton,[®] another heat-resistant polymer manufactured by DuPont, an evolved gas analysis (EGA) was developed by interfacing a mass spectrometer to a commercial thermogravimetric analyzer (TGA). TGA and mass spectrometric (MS) analyses can then be performed simultaneously, and the data combined and used for identification of small amounts of organic material in fiberglass media.

Experimental

At least one manufacturer of fiberglass filter media used in high-efficiency particulate air (HEPA) filter systems has recently replaced the controversial asbestos fiber reinforcement with heat-resistant, organic polymeric fibers. These fibers had been initially identified as a polyimide similar to Kapton,[®] manufactured by DuPont (see Figure 19), based on data from infrared (IR) spectroscopy, MS, and TGA analyses. This identification was discovered to be in error when Nomex[®] fibers, incorporated into a fiberglass media prepared at Rocky Flats, were also incorrectly identified as Kapton. Nomex is an aramid (aromatic polyamide) also manufactured by DuPont (see Figure 20).

The unique properties of these two DuPont polymers make identification by routine analytical methods extremely difficult. Both Kapton and Nomex are thermally stable to temperatures as high as 300 °C. Neither polymer is appreciably soluble in common laboratory solvents. The most promising method of separating the polymeric fibers from fiberglass media for analysis is based on the difference in decomposition temperatures between the polymers and fiberglass. The analytical methods initially employed rely on the thermal degradation of the polymeric fibers in order to separate them from the fiberglass and to obtain subsequent identification.

Infrared spectroscopy of the pyrolysis products of Kapton and Nomex proved to be a misleading identification tool. As illustrated in Figures 21 and 22, the IR pyrolyzate spectra of pure Nomex and pure Kapton differ considerably, which should provide for easy identification. However, the IR pyrolyzate spectrum of Nomex in fiberglass at low concentrations (see Figure 23) resembles that of

FIGURE 19. Structure of Kapton[®]: Poly N,N' - (p,p' - Oxydiphenylene)Pyromellitimide

FIGURE 20. Structure of Nomex[®]: Aromatic Polyamide

pure Kapton. The IR pyrolyzate spectra of both pure Kapton and of Nomex in fiberglass are indicative of ammonia (NH₃) and carbon dioxide (CO₂) condensed on the potassium bromide (KBr) IR window. This indicates that both pure Kapton and Nomex in fiberglass decompose completely, whereas pure Nomex, when pyrolyzed, decomposes with some of the organic molecule remaining intact.

TGA also proved an inadequate method for distinguishing between Kapton and Nomex based on their apparent decomposition temperatures. Kapton appears to decompose at 460 °C during TGA and Nomex at 370 °C. However, the apparent decomposition temperature of Nomex appears to increase, approaching that of Kapton as it is incorporated in low concentrations into fiberglass media.

Routine MS analysis also did not provide reliable data. Attempts to obtain MS data for samples of pure Kapton and pure Nomex by the solid probe method were unsuccessful. No detectable species

FIGURE 21. Infrared Pyrolyzate Spectrum of Nomex®

FIGURE 22. Infrared Pyrolyzate Spectrum of Kapton®

FIGURE 23. Infrared Pyrolyzate Spectrum of Fiberglass Filter Media Containing 5 Weight Percent Nomex®

were produced from Kapton in the probe temperature range (i.e., ambient to 400 °C). Under these conditions, Nomex evolved the thermal decomposition products NH_3 , sulfur dioxide. Phenylene diamine was produced when the sample was heated to just over 400 °C, which is above the controlled-temperature range for probe analysis. Because of the incomplete nature of the MS information obtained from direct probe analysis of the two polymers, an alternative method of sample decomposition was sought. This search resulted in the pairing of thermal and MS analytical methods into an evolved-gas analysis (EGA) method.

TGA provides the means of heating a sample to temperatures as high as 1000 °C to decompose and volatilize that sample. If the volatile decomposition products can then be routed to the chamber of a mass spectrometer, these products can be identified by MS analysis. For these analyses, a

DuPont 951 thermogravimetric module was interfaced into a portable quadrupole mass spectrometer, and the entire system was evacuated. Scans of the gaseous thermal-decomposition products produced during TGA were recorded at intervals of 100 °C. Additional scans were recorded at the critical decomposition temperature of each sample.

The gaseous decomposition products of Kapton and Nomex are similar but show some variations which may be useful in distinguishing between the two materials. Carbon dioxide is the major decomposition product for both materials even under semi-vacuum conditions (less than 4 torr). Both Kapton and Nomex produce NH_3 . The NH_3 becomes a major component in the Kapton EGA at temperatures of 700 °C and greater. Nomex produces NH_3 at 600 °C. The only significant organic component resulting from the decomposition of Kapton is phenol. In addition, trace amounts of

TABLE 3. Analytical Data for Kapton® and Nomex®

Method of Analysis	Results of Analyses	
	Kapton®	Nomex®
Infrared Spectroscopy	The pyrolyzate spectrum resembles that of ammonium ion with additional aromatic characteristics of low intensity.	In concentration of 20 percent or greater, the pyrolyzate spectrum resembles that of nylon with additional aromatic character.
Thermogravimetric Analysis	TGA decomposition onset temperature (in air) is 460 °C.	TGA decomposition onset temperature of pure Nomex (in air) is 370 °C; 20 percent Nomex in fiberglass is 400 °C; 5 percent Nomex in fiberglass is 430 °C.
Evolved Gas Analysis	EGA yields CO ₂ (major), NH ₃ (major at 700 °C and greater), phenol, and trace amounts of benzene, toluene, aniline, and cyanobenzene.	EGA yields CO ₂ (major), NH ₃ (major at 600 °C and greater), benzene, toluene, aniline, cyanobenzene, trace of methylcyanobenzene, and large quantities of SO ₂ and CS ₂ .

benzene, toluene, aniline, and cyanobenzene are detected in the Kapton decomposition products. The decomposition of Nomex produces greater relative amounts of organic components than that of Kapton. Benzene, toluene, aniline, and cyanobenzene are all noted in significant quantities during EGA of Nomex. In addition, a trace amount of methylcyanobenzene is detectable. Nomex also yields large quantities of SO₂ and carbon disulfide (CS₂) during thermal decomposition. These two sulfur-containing components, presumably originating from a proprietary additive or process chemical, are not detectable in the EGA of Kapton.

EGA data can be used, in addition to data obtained from complimentary methods, to distinguish between Kapton and Nomex should either be suspected of being present in a sample of fiberglass filter media. Table 3 summarizes the analytical data for Kapton and Nomex as obtained from the methods herein discussed.

X-RAY FLUORESCENCE SPECTROSCOPY

BERYLLIUM DENSITY PROBLEM

Jack L. Long

Summary

A relationship between density differences of beryllium (Be) metal has been attributed to the presence

of bromine (Br) or bromide ion (Br⁻). The presence of Br, initially detected by spark-source mass spectrometry (SSMS), has been verified by X-ray fluorescence techniques.

Experimental

Regions of varying densities in metallic beryllium (Be) have been detected by radiography. Recently, this phenomenon was observed in powder-pressed material. Metallographic examination by optical microscopy and scanning electron microscopy techniques were not effective in explaining the density differences. SSMS results indicated that the Br or Br⁻ concentration was higher in the high density regions than in the lower density regions. Energy dispersive X-ray fluorescence spectroscopy was used to confirm the SSMS results.

The X-ray fluorescence analysis indicated the presence of Br, as verified by the appearance of both the K_α and K_β lines of Br in the energy dispersive spectra. Repetitive determinations near the craters formed by the spark source mass spectrometer beam in the high and low density regions revealed a significant difference in Br concentration by a factor of two. X-ray scans lengthwise across the specimen showed Br concentration differences up to a factor of six. Furthermore, starting at one end of the sample, the Br concentration was at a

relatively low value, rose to a relatively high value, then decreased to an intermediate value.

A specimen of normal Be metal was analyzed by X-ray fluorescence spectroscopy for comparative purposes. The Br peak was not significantly different from background. Thus, the presence of Br in Be metal having abnormal density variations has been verified in this investigation and has been shown to be of significantly higher concentration in the high density region.

NIObIUM IN URANIUM-NIObIUM ALLOYS

Jack L. Long

Summary

A procedure was developed for the X-ray fluorescence determination of niobium in uranium-niobium (U-Nb) alloys. The procedure requires only that a compact be made from turnings, thus avoiding wet-chemical treatment entirely. By eliminating the wet chemistry, a time-savings factor of at least three is obtained over the method previously used. The standard deviation of Nb-U ratios obtained from the compacts is smaller than that obtained from the aqueous method on a series of duplicate aliquot analyses.

Experimental

Previously, U-Nb alloys had been analyzed routinely by weighing 8 to 25-gram aliquots and preparing these aliquots for X-ray fluorescence analysis by a lengthy dissolution treatment, which included evaporation, additions of acids, hydrogen peroxide, and oxalate, and several cooling steps. The large aliquot size was used because inhomogeneities with respect to Nb are common in U-Nb alloys when the Nb content approaches six percent. The subsequent X-ray fluorescence analysis on the liquid sample contained by a Mylar® window consisted of determining the number of counts per twenty seconds of the $U_{L\gamma}$ and the $Nb_{K\beta}$ peaks. The ratio, $Nb_{K\beta}$ counts/ $U_{L\gamma}$ counts, then was compared to a calibration curve made by counting aqueous standards containing varying amounts of Nb and

U. The new procedure, which employs solid compacts, eliminated dissolution, preparation of aqueous standards, chemical solution makeup, potential contamination resulting from sample-container rupture, and the recovery of U from the liquid samples.

The feasibility of using solid compacts was established by determining U-Nb ratios on single strands of machined turnings and preparing a compact from many strands. Single strands from the same piece resulted in varying ratios, while repetitive counts of the compact were reproducible within the established limits of error. The greatest obstacle to the procedure was the preparation of standards because of the inhomogeneity problem. The standards were prepared by the following procedure. Castings were made containing from 5.0 to 6.6 percent Nb. Between 20 and 40 grams of turnings were machined from each casting. Each batch of turnings was separated into individual strands and approximately one-third of each strand was cut off. Thus, each batch was divided into two portions. The smaller portion was used for Nb analyses by the conventional wet chemical method, while a compact was made from the larger portion. Four determinations were made on each wet chemical portion and the results averaged.

Compacts were made by pressing 10 to 30-gram portions in dies. Usable compacts could be pressed with pressures in the range of 20,000 to 50,000 pounds per square inch (psi), but the higher pressures yielded a better compact. The results discussed in the following text were obtained with compacts pressed at 40,000 to 50,000 psi.

The percent Nb results and corresponding count ratios for seven standards are given in Table 4. The mean standard deviation of the mean Nb-U count ratio of all seven data sets is 0.0027, and the mean relative standard deviation is 0.90 percent. Figure 24 shows the least squares plot of Nb concentration as a function of the count data. The correlation coefficient for this data is 0.999, but the correlation coefficient using three count ratios for each standard has always been 0.995 or greater. Furthermore, the fact that the count data in Table 4 were taken over a period of two months indicates a stable and reproducible system.

TABLE 4. Niobium-Uranium (Nb-U) Ratios as a Function of Niobium Concentration

Niobium Concentration (Weight Percent)	Mean Nb-U Ratio*	Standard Deviation	Relative Standard Deviation (Percent)
5.07	0.264	0.0028	1.06
5.17	0.269	0.0030	1.12
5.43	0.277	0.0021	0.76
5.56	0.282	0.0018	0.64
5.94	0.299	0.0026	0.87
6.22	0.310	0.0031	1.00
6.61	0.327	0.0032	0.98

*Average of 14 duplicate determinations.

FIGURE 24. Least-Squares Plot of Niobium Concentration as a Function of X-Ray Fluorescence Count Data on Uranium-Niobium Alloy Compacts

The reproducibility of duplicate determinations of U-Nb ratios is considerably better for the compact samples than for the aqueous samples. For 125 samples prepared by the wet-chemical procedure, the mean of the differences of ratios for duplicate aliquots was 0.0071 with a standard deviation of 0.0068. For 52 compacted samples analyzed directly, the mean of the differences of ratios for duplicate determinations was 0.00192 with a standard deviation of 0.00156. Thus, at least a threefold improvement in precision between replicate analyses on a given sample is anticipated when it is prepared by compaction rather than by the previously-used wet chemical steps.

The high precision of the compact procedure has resulted in attempts to correlate Nb results in adjacent regions of sections cut from a single casting. This type of correlation had been unsuccessful when the aqueous aliquot method was employed. Preliminary results with compacts look promising, although the study has not been completed.

MISCELLANEOUS PROJECTS

PLUTONIUM-INDUCED REACTIONS OF NITRIC ACID-ETHYLENE GLYCOL MIXTURES

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Summary

Mixtures of ethylene glycol, water, and nitric acid, which are relatively inert under typical laboratory storage conditions, readily undergo decomposition reactions when significant amounts of plutonium (Pu) [i.e., 5 grams per liter (g/l)] are present in the solution. A major reaction product when Pu is present has been characterized as a polymeric acrylic ester having the structure $(\text{CH}_2\text{CHCOOR})_n$, where $\text{R} = \text{CH}_2\text{OH}$ or $\text{CH}_2\text{CH}_2\text{OH}$ groups. The nature of this product indicates that oxidation, polymerization, and alcohol-carboxylic acid

esterification reactions predominate over the alcohol-nitric acid esterification (alkyl nitrite formation) reaction which normally occurs under nonradiolytic conditions. Furthermore, the product suggests a free-radical mechanism that is typical of radiolysis; however, no gamma-irradiation experiments with Pu absent were performed to confirm a radiolysis mechanism.

Experimental

Reactivity and compatibility assessments of mixtures of two or more substances are routinely performed at Rocky Flats by differential thermal analysis (DTA) of the mixtures contained in sealed quartz-capillary tubing (refer to earlier Progress Report, RFP-1888, May 31, 1972, page 11). Assessments of ethylene glycol-nitric acid (HNO_3) mixtures have been performed in the past because of the use of both materials in Pu-production areas (viz., ethylene glycol as a heat-exchange agent and HNO_3 as a dissolution medium) and the potential for inadvertent contact between one another. DTA results, summarized in Table 5, reveal that, for mixtures of ethylene glycol and HNO_3 , a reaction exotherm occurs only after the boiling point of HNO_3 , of 86°C , has been exceeded. Previous work of characterizing the reaction products of equal volume mixtures of HNO_3 and common alcohols, including ethylene glycol, indicates the HNO_3 -esterification reaction (i.e., the nitration reaction proceeding by way of a unimolecular-nucleophilic-substitution mechanism) predominates over a simple oxidation reaction (refer to earlier Progress Report, RFP-2699, March 27, 1978, pages 16-17).

During the course of additional routine reactivity-hazard assessments of 8 and 12M HNO_3 with aqueous ethylene glycol, one of the mixtures, which contained 11.5 volume percent production ion-column eluate and stored in a sealed, air tight polypropylene container, pressurized and ruptured the container. Significant amounts of sludge were found in the remains of the solution. This sludge, which had the consistency of molasses or thick corn syrup, was dried at 80°C for 24 hours to evaporate residual water and HNO_3 , then examined by infrared spectroscopy for structural elucidation.

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TABLE 5. Sealed-Capillary Differential-Thermal-Analysis
Results for Aqueous Ethylene Glycol-Nitric Acid Mixtures

Solution	Reaction Exotherm Onset Temperature (°C) ^a
Equal volume mixture of 8M nitric acid (HNO ₃) and 1:1 aqueous ethylene glycol	122 ± 1
Equal volume mixture of 12M HNO ₃ and 1:1 aqueous ethylene glycol	117
Equal volume mixture of 8M HNO ₃ and ethylene glycol	127 ± 7
Production ion-column eluate ^b	none observed
Equal volume mixture of production eluate and 16M HNO ₃	none observed
Equal volume mixture of production eluate, 8M HNO ₃ , and 1:1 aqueous ethylene glycol	98 ± 8
Mixture of 11.5 volume percent production effluent in equal volumes of 8M HNO ₃ and 1:1 aqueous ethylene glycol (<i>reactive effluent</i>)	98
Equal volume mixture of <i>reactive effluent</i> and 16M HNO ₃	88
Mixture of 50 volume % <i>reactive effluent</i> , 25% 8M HNO ₃ , and 25% 1:1 aqueous ethylene glycol	62 ± 4

a. ± results represent the mean standard deviation of replicate DTA trials.

b. Eluate consists of approximately 0.35M HNO₃ and a Pu concentration of 5 grams per liter.

c. Effluent consists of approximately 7M HNO₃ and a Pu concentration of 10⁻⁴ grams per liter.

The sludge was primarily organic in nature and characterized as a polymeric acrylic resin having the structure (CH₂CHCOOR)_n where R = CH₂OH or CH₂CH₂OH groups. Neither ethylene glycol nor its anticipated oxidation product, oxalic acid, was detected in the sludge. Furthermore, there was no evidence in the sludge of nitration products (such as alkyl nitrites), carboxylates (i.e., Pu salts of carboxylic acids), or inorganic nitrate salts.

Emission spectroscopy determination of the dried sludge indicated a Pu content of just 1.6 weight percent, suggesting impurity levels of the metal rather than formation of a Pu-organometallic species. The composition of the sludge suggested that it was the product of free radical-induced oxidation, polymerization, and alcohol-carboxylic acid esterification reactions rather than the HNO₃-esterification reaction that would predominate under nonradiolytic

conditions. The resultant polymeric product showed no further instability upon heating and combusted in a relatively mild manner when muffled at 600 °C.

To test the hypothesis that the reaction was induced by Pu and not some other impurity, a synthetic feed solution, consisting of 8M HNO₃ and a significant concentration of dissolved Pu (5 g/l), was contacted with an equal-volume mixture of ethylene glycol and water and observed to react in a similar manner within 48 hours. DTA experiments were then performed with ion-column eluate and effluent samples of production feed solutions mixed with ethylene glycol and water.

The DTA data in Table 5 indicate: (1) exothermic reactions occur only when ethylene glycol is present in the system; (2) the exotherm onset temperatures decrease when additional HNO₃ or aqueous ethylene glycol is added to the system; and (3) the exotherm onset temperatures are substantially lower for the Pu-containing solutions than for the solutions without plutonium. The third observation is evidence that the reaction is radiolytically induced by the plutonium.

The results of this investigation demonstrate the need to consider the effects of the presence of radioactive materials in performing reactivity assessments of systems which may contain, either deliberately or inadvertently, significant concentrations of radioactive materials. In this instance, a closed system, containing 11.5 volume percent aqueous solution with a Pu concentration of 5 g/l, reacted significantly within 48 hours, whereas the same system devoid of the Pu-containing solution would be inherently stable at room temperature, perhaps, for years.

OXYGEN IN CHROMIUM RECOVERY STUDY

Karl N. Kirchner

Summary

The effect of platinum as a flux was studied in the determination of oxygen in chromium metal by

TABLE 6. Gas-Fusion Analysis of Chrome Rod for Oxygen in the Presence and Absence of Platinum Flux

Platinum-Chromium Ratio (By Weight)	Number of Aliquots	Mean Oxygen Concentration (parts per million by weight)*
3:1	6	3060 ± 224
10:1	8	3947 ± 242
No Platinum	12	3199 ± 282

*The ± results are the 95 percent confidence intervals for replicate trials (±2 means standard deviations).

fusion analysis. No significant differences in oxygen results were observed for analyses performed with or without the platinum flux.

Experimental

The oxygen content of a chromium sample (chrome rod No. 35A) was determined using a LECO® TC-30 Nitrogen-Oxygen Determinator. The current procedure called for adding platinum (Pt) to the chromium (Cr) sample in a 3 to 1 by weight ratio. In this study, three series of experiments were performed: those in which the 3 to 1 Pt-Cr ratio was used, those in which a 10 to 1 Pt-Cr ratio was used, and those in which Pt was absent as a flux. The chrome sample size for these trials remained constant at approximately 0.1 gram.

The results of the study are summarized in Table 6. No apparent differences were noted in the results regardless of whether Pt was present. As a result of this study, oxygen in Cr is now determined by this method without the use of a Pt flux.

CHLORIDE AND SULFATE IN WATER-SOLUBLE OILS

Amelia M. Miller

Summary

With the use of specific-ion electrodes, aqueous solutions of water-soluble emulsion type oils, such as Texaco Soluble D, can be analyzed for chloride

(Cl^-) and sulfate (SO_4^{2-}). By the method of standard additions, Cl^- can be determined as low as 2 parts-per-million, and SO_4^{2-} , by means of a Grans plot titration, can be determined above 100 parts-per-million.

Experimental

Water-soluble oils, such as Texaco Soluble D, are routinely employed as corrosion inhibitors and lubricants for various machinery at Rocky Flats. Impurities such as sulfate and chloride in the corrosion inhibitor can cause stress-corrosion cracking and therefore need to be determined. The use of specific-ion electrodes enables a rapid, accurate means of monitoring these solutions for a buildup of these impurity ions.

For Cl^- analysis, 25 milliliters (ml) of the aqueous oil emulsion is acidified with 5 ml of concentrated nitric acid and diluted to 50 ml. The Cl^- is then determined by the method of standard addition with chloride specific-ion electrode. For the SO_4^{2-} analysis, 5 ml of the aqueous oil emulsion is diluted to 50 ml with distilled water, and 50 ml of methanol is added. A lead electrode, a double-junction reference electrode with other filling solution of 1 normal sodium nitrate, and titrant of 0.01 molar lead perchlorate are used for Grans plot titration of SO_4^{2-} .

DECONTAMINATION OF SURFACE COATINGS

Douglas L. Scott

Summary

In designing a new size-reduction facility for construction at Rocky Flats, a coating for walls, floors, and other surfaces, which would be easy to decontaminate periodically, was desired. Samples of eight potential coatings of commercially-available paint on 1.5 by 1.5 inch coupons and a stainless steel coupon for comparison were submitted to the Radiochemistry Laboratory. The ability to decontaminate these coatings varied widely, with

decontamination factors (DF) ranging from a low of 0.82 to a high of 94.5. All compared unfavorably to stainless steel, which had a DF of 1600.

Experimental

The decontamination procedure given in American National Standards Institute (ANSI) N5 12-1974 was used with minor modifications which were necessitated from working with plutonium (Pu). The contaminating solution was made up in 2 normal (N) nitric acid (HNO_3) to avoid precipitating Pu. An activity of approximately 5×10^5 disintegrations-per-minute per 100 microliters (μl) of solution, a factor of 10 lower than the standard, was deemed necessary as the counting was to be performed outside the glovebox system.

Three samples of each paint coating were contaminated by pipetting 200 μl of 2N HNO_3 solution, containing 0.0485 gram-per-liter (g/l) Pu, onto each coupon. The coupons were air-dried, and the alpha-particle activity measured using a flow proportional detector. Each coupon was subsequently washed, air-dried, and counted three times. The first washing was performed in room temperature tap water. The second and third were performed in an aqueous mixture of 0.4 molar (M) oxalic acid, 0.05M sodium fluoride, and 0.03M hydrogen peroxide at room temperature (approximately), 24 °C and 60 °C, respectively.

The ability to decontaminate each coating was compared by calculation of the overall DF, defined as the ratio of the activity before washing to the activity after the final washing. For the coatings tested, the DF's ranged from 0.82 to 94.5 compared to 1600 for stainless steel. The relatively poor performance of the coated surfaces is attributed to the reaction of the coatings with the acidic contaminating solution. Six of the coatings showed appreciable discoloration in the contaminated area, and one had slight discoloration. The final coating showed no discoloration and yielded the highest DF, 94.5, versus an average of 1.12 for the other seven coatings. DF's of less than 1.00 resulted from masking the count at the surface by a thin film of paint constituents that migrated after separation from the bulk coating.