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MASTER

QUALITY ENGINEERING AND CONTROL
SEMIANNUAL PROGRESS REPORT
MAY THROUGH OCTOBER 1976

SERVICE LABORATORIES GROUP

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U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
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SUBJECT DESCRIPTORS

Absorption Spectroscopy
Electrochemistry
Emission Spectroscopy
Gas Analysis
Gas Chromatography
Infrared Spectroscopy
Phosphoric Acid Esters
Plutonium
Reaction Kinetics
Sampling
Solvent Extraction
Waste Processing

**ROCKWELL INTERNATIONAL
ATOMICS INTERNATIONAL DIVISION
ROCKY FLATS PLANT
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SERVICE LABORATORIES GROUP

Herman C. Anderson

ABSORPTION SPECTROSCOPY

SILICON IN STEELS AND PLUTONIUM-SILICON ALLOYS

Roger S. Cichorz

Summary:

A feasible spectrophotometric method for the determination of silicon (Si) involves formation of silico-12-molybdate, $(\text{SiMo}_{12}\text{O}_{40})^{4-}$, in acidic solution and measurement of the absorbance of this complex at a suitable analytical wavelength such as 400 or 410 millimicrons ($m\mu$).¹ The silico-12-molybdate spectrophotometric method has been applied to high Si-content steels of the National Bureau of Standards (NBS), (Washington, D.C.), to assess the accuracy of the method associated with determination of Si in other metals. The analysis results of the spectrophotometric method on plutonium metal samples have been compared to results obtained by emission spectrographic analyses. In general, agreement between the two methods is noted over the 0.1 to 2.5 weight-percent Si-content range.

Experimental:

In processing the NBS steel standards, the removal of iron (Fe) by ion exchange, extraction, or precipitation techniques is not practical, since Fe is the major matrix component. Consequently,

a method developed by Hill,² in which Si is determined directly in the presence of Fe, was adapted to these steels.

In the modified Hill procedure, weighed samples of the NBS steels were dissolved in hydrochloric acid (HCl), treated with permanganate solution in order to oxidize Fe^{2+} to Fe^{3+} , and treated with hydrofluoric acid (HF) to complex Fe^{3+} as FeF_6^{3-} . The excess HF, which interferes with the spectrophotometric method, was removed by complexation with boric acid. In spite of relatively high absorbance readings of the blanks, probably caused by chlorine resulting from permanganate oxidation of HCl, excellent agreement with the NBS values was achieved with this procedure.

The direct spectrophotometric determination of Si in the presence of Fe is subject to erroneously high results because of enhancement by Fe^{3+} . The direct method, however, appears applicable to metal matrices other than Fe, and has been successfully applied to Fe-free Pu-Si alloys. The results obtained from the modified Hill and direct spectrophotometric procedures are summarized in Table I.

Plutonium alloys containing from 0.1 to 2.5 weight percent Si were analyzed by the direct spectrophotometric method. The procedure involved dissolving weighed amounts of freshly brushed metal in 6M HCl and treating with 48 percent HF in order to precipitate Pu^{3+} as plutonium(III) fluoride (PuF_3) and to render the Si soluble as fluosilicic acid (H_2SiF_6). After

¹H. R. Shell. "Silicon," Pages 107-206. *Treatise on Analytical Chemistry*, Part II. Volume 2. I. M. Kolthoff and P. J. Elving, Editors. Interscience Publishers, New York. 1962.

²U. T. Hill. "Colorimetric Determination of Silicon in Low Alloy and Carbon Steels." *Analytical Chemistry* 21:589. May 1949.

TABLE I. Spectrophotometric Silicon Results for National Bureau of Standards Steels.

NBS Standard Steel No.	NBS Value Silicon (weight percent)	Modified Hill Procedure		^a Direct Determination	
		Silicon Found	^b RSD (percent)	Silicon Found (weight percent)	^b RSD (percent)
82-a	2.07	2.09	5.1	3.14	38.7
125-a	3.32	3.33	1.7	4.41	6.9

^a Silico-12-molybdate complex formation in the direct presence of Fe(III).

^b The relative standard deviations (RSD) are calculated from the results of six analyses performed by each method.

TABLE II. Determination of Silicon in Plutonium-Silicon Alloys.

Sample	Spectrophotometric		Emission Spectrographic	
	Silicon (weight percent)	^a RSD (percent)	Silicon (weight percent)	^a RSD (percent)
1	0.13	—	^b 0.16	9.1
2	0.25	2.5	0.28	6.2
3	0.51	—	0.52	17.3
3	1.00	5.0	—	—
4	1.65	0.5	^c 2.11	5.0
5	2.04	2.1	2.48	0.9

^a Relative standard deviations (RSD) are given when replicate analyses were performed on a sample.

^b Samples 1, 2, and 3 were analyzed by the *KOH Method* in which the Si was isolated as the fluosilicate species and treated with potassium hydroxide to prevent volatilization as silicon tetrafluoride during the excitation process.

^c Samples 4 and 5 were analyzed by a germanium-silicon dioxide internal standard technique.

removal of the precipitate, the resulting H_2SiF_6 solution was treated with aqueous 2 percent boric acid to complex excess HF and quantitatively diluted to 100 millilitres.

Aliquots of the solutions were taken, the silico-12-molybdate species formed, and Si concentration

determined by measuring the absorbance at 400 and 410 $\text{m}\mu$ on a conventional ultraviolet-visible spectrophotometer and comparing to standards via Beer-Lambert calibration plots.

Results obtained on these alloys by both the spectrophotometric and emission spectrographic methods³ are summarized in Table II. In the initial spectrophotometric trials, Samples 1, 2, and 3 were determined with insufficient boric acid added to remove interferences by HF, and as a consequence incomplete color development of the silico-12-molybdate complex occurred and low results were probable. Sample 3 then was analyzed involving excess boric acid, and a higher, more accurate Si result was obtained. Samples 4 and 5 were analyzed similarly; no HF interference was noted, and apparent quantitative color development occurred on silico-12-molybdate formation.

The analytical results for the spectrophotometric method may be low if silicon tetrafluoride (SiF_4) is allowed to escape as a gas during HF treatment or if physical entrapment of the Si species occurs during precipitation. To avoid release of SiF_4 , solutions are chilled with ice prior to addition of HF. To avoid loss of Si in the PuF_3 precipitate, it is necessary to wash the precipitate thoroughly with dilute HF and combine the wash solution with filtrate prior to analysis.

KINETICS INVESTIGATION OF THE EFFECT OF FLUORIDE ION ON SILICO-12-MOLYBDATE

Roger S. Cichorz

Summary:

The kinetics of the decomposition of the silico-12-molybdate complex, $(\text{SiMo}_{12}\text{O}_{40})^{4-}$, by hydrofluoric acid (HF) attack over the range of pH 1.0 to 1.5 have been investigated spectrophotometrically. The absorbance decrease of this

³ Robert A. Sandberg, Rocky Flats Plant. Private Communication. October 1976.

TABLE III. Rate of Absorbance Decrease
Due to Hydrofluoric Acid-Induced Decom-
position of the Silico-12-Molybdate Species.

Hydrofluoric Acid Concentration [HF]	*Silicon Concentration [Si] = 4.7 grams per litre		*Silicon Concentration [Si] = 9.4 grams per litre	
	400 (millimicrons)	410 (millimicrons)	400 (millimicrons)	410 (millimicrons)
0.10M	1.208	0.8578	—	—
0.20M	4.006	2.924	7.637	6.181
0.40M	17.78	13.04	35.61	26.88
0.60M	38.52	29.98	66.53	47.03

*Results are expressed in (decrease in absorbance
units $\times 1000$) per minute ($\Delta A \cdot 10^3 \cdot \text{min}^{-1}$).

species at 400 and 410 millimicrons ($m\mu$) with respect to time follows third-order kinetics, the rate of complex destruction being proportional to the first order of $(\text{SiMo}_{12}\text{O}_{40})^{4-}$ concentration and to the second order of HF concentration.

Experimental:

The purpose of this investigation was to obtain information on the effects of fluoride-ion (F^-) interference on the formation and destruction of the silico-12-molybdate complex, which is used in colorimetric determinations either directly or as the intermediate for the reduced silicomolybdate blue species. Low concentrations of F^- have little effect on $(\text{SiMo}_{12}\text{O}_{40})^{4-}$, according to previous investigators;⁴ however, at excessive concentrations, F^- has been found to interfere with the colorimetric procedure.

The silico-12-molybdate complex is prepared in the pH range of 1.0 to 1.5 from a standardized solution of silica by acidifying an aliquot of the standard with dilute hydrochloric acid (HCl) and adding aqueous 10 percent ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$. Maximum color development of this complex occurs in from 7 to 10 minutes.

The resultant complex is then added to a stock solution of F^- , buffered with HCl to a pH of from 1.0 to 1.3, and quantitatively diluted to 100 millilitres. The F^- in this pH range is completely associated as HF. In these experiments, the concentrations of silicon (Si) and F^- are known and can be varied for purposes of obtaining kinetics data.

It has been determined that HF concentrations of less than 0.10M have little effect on $(\text{SiMo}_{12}\text{O}_{40})^{4-}$ in the pH range of 1.0 to 1.5. In the Si concentration range of 4.7 to 14.0 milligrams per litre, the decomposition of $(\text{SiMo}_{12}\text{O}_{40})^{4-}$ has been found to follow a third-order rate expression. The decomposition-reaction rate at the 95 percent confidence level is:

$$-\frac{d[(\text{SiMo}_{12}\text{O}_{40})^{4-}]}{dt} = [\text{Si}]^{0.940 \pm 0.193} [\text{HF}]^{2.045 \pm 0.216}$$

A summary of the kinetic data, determined spectrophotometrically by examining the absorbance decrease at 400 and 410 $m\mu$, is given in Table III. It has been determined previously that the absorbance of $(\text{SiMo}_{12}\text{O}_{40})^{4-}$ at 400 and 410 $m\mu$ in

⁴Shell. *Op. cit.* Page 113.

Legend

Silicon and Hydrofluoric Concentrations--

- -- 9.4 milligrams per litre (mg/l), 0.6M (molarity).
- -- 4.7 mg/l, 0.6M.
- △ -- 9.4 mg/l, 0.4M.
- ▲ -- 4.7 mg/l, 0.4M.
- -- 9.4 mg/l, 0.2M.
- -- 4.7 mg/l, 0.2M.
- ◇ -- 4.7 mg/l, 0.1M.

FIGURE 1. Change in Absorbance (decrease in concentration of silico-12-molybdate complex) versus Time.

the pH range of 1.0 to 1.5 is directly proportional to Si concentration, so that the rate of absorbance decrease is, in effect, the rate of $(\text{SiMo}_{12}\text{O}_{40})^{4-}$ decomposition. Typical plots of the change in absorbance due to $(\text{SiMo}_{12}\text{O}_{40})^{4-}$ decomposition

with time are given in Figure 1. The absorbance changes have been corrected for the normal time-related fading observed after complex formation.

ELECTROLYSIS

REMOVAL OF PLUTONIUM FROM PROCESS WASTE STREAMS

Jack L. Long

Summary:

Electrolysis experiments involving the removal of plutonium (Pu) from neutral and alkaline solutions were continued, and the relationship between Pu removal and the pH of the electrolytic solutions was established. These investigations were made on synthetic process-waste-stream solutions over the pH range of 9.1 to 13.7.

Experimental:

Synthetic aqueous process-waste-stream solutions were prepared containing 1711 grams per litre (g/l) sodium nitrate, 3.5 g/l sodium fluoride, and 8.0×10^{-8} g/l Pu. Sodium hydroxide was used to make pH adjustments. These solutions were electrolyzed for 2.0 hours at a current of 0.60 amperes with an applied potential of approximately 3.2 volts. The same platinum-gauze anode and cathode were used for each experiment. Between experiments, the electrodes were leached twice with aqueous 10 percent nitric acid to remove residual Pu. In every case, the second leach solution contained negligible Pu.

The variation in Pu concentration with pH of the synthetic process solutions after electrolysis is depicted graphically in Figure 2. The data are nonlinear and appear to form a curve with the exception of pH = 13.7. More experiments are needed to determine if a downward trend occurs in the pH range of 13.0 to 14.0, or if the pH = 13.7 result is an anomaly. From the present experiments,

FIGURE 2. Plutonium Content of Electrolyzed Product Solutions as a Function of pH.

it is concluded that the optimum pH for obtaining product with the lowest concentration is at or near 11.0.

EMISSION SPECTROMETRY

PLASMA-SOURCE ANALYSIS OF ELEMENTS IN STEEL

Ann C. Ficklin

Summary:

The Spectraspan-III Plasma Jet spectrometer (Spectrametrics, Inc., Andover, Massachusetts) has a multi-element capability which is being used to determine nine elements in steels with the accuracy and sensitivity of single-element atomic absorption spectroscopy analysis. The elements

include nickel, chromium, titanium, manganese, copper, silicon, molybdenum, phosphorus, and aluminum.

Experimental:

The Spectraspan-III Plasma Jet is an echelle-grating optical emission spectrometer with a plasma source. The direct-reading, multi-element capability cuts analysis time by half without sacrificing any of the sensitivity of atomic absorption spectroscopy analysis.

Solutions as concentrated as 50 grams per litre (g/l) may be efficiently pumped into the Plasma Jet. Using a 50-g/l steel solution, the minimum detection limits are 25 parts per million (ppm) by weight for phosphorus (P) and 5 ppm for aluminum (Al).

Fifteen steel samples were analyzed by atomic absorption spectroscopy and the Plasma Jet for Al. The results showed agreement between the two methods to within ± 10 relative percent of the amount of Al present. The Plasma Jet results on eight samples agreed with the results from the approved method of the American Society for Testing and Materials (ASTM) for phosphorus analysis within ± 7 relative percent.

The Plasma Jet results for chromium and nickel on two stainless steel samples were checked by comparing with results obtained by an ASTM-approved method. The agreement was within ± 4 relative percent for chromium and ± 2 relative percent for nickel. Silicon was analyzed by atomic absorption spectroscopy and by Plasma Jet in twelve steel samples. Results agreed within ± 8 relative percent.

Standard reference materials from the National Bureau of Standards (NBS) were used as the standards on these comparisons. The type of steel has no effect on the analysis of these elements, but the salt content of the samples and the standards must be the same or there would be a significant matrix effect. Samples and standards were dissolved in hydrochloric and nitric acids. If a silicon analysis were required, hydrofluoric

acid was also added. Experience with the Plasma Jet instrument at present has been with the nine elements described. However, this instrument has a 20-element determination capability on the direct reader.

GAS CHROMATOGRAPHY

METHOD FOR WATER IN ACETONE

Karl N. Kirchner

Summary:

A standard-addition gas chromatography method has been established to determine the water content of reagent-grade acetone with a minimum detection limit of 0.005 weight percent. The method is employed as a quality control procedure to assure users that the acetone does not exceed the maximum allowable water content of 0.5 percent, specified in a Rocky Flats Plant Quality Control Procedure and by the American Chemical Society for reagent-grade acetone.⁵

Experimental:

Ordinarily, the Karl Fischer method is used for the determination of water in organic solvents. Acetone and other ketones, however, interfere with this method, necessitating the development of an alternative means of analysis. Gas chromatography appeared feasible because separation of water and acetone can be effected with an appropriate column.

Standards for the gas chromatography method are prepared by adding a known amount of water to the aliquot of acetone to be analyzed. The sample spiked with water and the untreated sample are injected into a gas chromatograph equipped with

a Porapak® Q-column (Waters Associates) at 200 °C and a thermal-conductivity detector. With these operating conditions, the water elutes from the column prior to the acetone. The gas chromatogram is obtained, and the water concentration can be calculated from the peak heights according to the following equation:

$$C_s = \frac{H_s \cdot C_m}{(H_m - H_s)}$$

Where:

C_s = the concentration of water in the reagent

H_s = the peak height of the reagent

H_m = the peak height of the spiked sample

C_m = the concentration of
water added to the spiked sample

The minimum detection limit of water for a typical sample aliquot of 10 microlitres is 50 parts per million by weight. The relative standard deviation of acetone samples containing 0.5 percent water is approximately 8 percent. For this application, standards have been prepared in the concentration range of from 0.005 to 1.5 percent, although water contents of greater than 1.5 percent can be determined by this method.

DETERMINATION OF PLASTICIZER IN AIR

Virgil H. Matzick

Summary:

A gas chromatographic method⁶ has been adapted to determine the concentration of bis(2-ethylhexyl) phthalate in room air. The bis(2-ethylhexyl) phthalate, known as commercial dioctyl phthalate

⁵ *Reagent Chemicals, American Chemical Society Specifications*. Fifth Edition. American Chemical Society, Washington, D. C. 1974. Page 56.

⁶ OSHA Method S40, validated January 17, 1975. U. S. Department of Health, Education and Welfare for Occupational Safety and Health Administration, Cincinnati, Ohio. May 1975.

(DOP), is used extensively at the Rocky Flats Plant in the shipping-box fiberglassing operation and in the respirator fitting chamber. Analyses have been performed on air samples of from 0.5 to 30 litres in volume containing DOP concentrations of from <0.2 to 25 milligrams per cubic metre (mg/m^3).

Experimental:

The sampling involves drawing a known volume of air through a cellulose-membrane filter to trap the organic aerosol present in the atmosphere. The filter is then folded and placed in a 1-dram glass vial, and 1 millilitre carbon disulfide is added to the vial. The vial is agitated for approximately 30 minutes on a shaker table to extract any DOP present on the filter paper. A 1-microlitre aliquot of the extractant solution is then analyzed by gas chromatography using flame-ionization detection. Concentrations are determined by comparing peak heights or areas of the sample versus peak heights or areas of calibration standards.

Calibration standards are prepared by weighing given amounts of DOP in volumetric flasks and bringing to volume with carbon disulfide. Generally, three standard solutions covering the expected level of concentration of DOP in the samples are prepared. The control standard for extraction efficiency should contain a concentration of DOP in the range of one of the calibration standards.

Extraction efficiencies are determined by pipetting known volumes of control standards on filter papers and allowing to dry. These filter papers are then analyzed in the same manner as the samples. In general, the extraction efficiencies have been between 85 and 90 percent for the control standards, so a correction factor of 1.1 to 1.2 is applied to the results to insure quantitative recoveries. Reproducibility of the chromatograms is estimated to be within ± 2 relative percent on a series of runs of the same control standard. A series of samples originating from the box-coating operation have been analyzed by this method and have had DOP concentrations ranging from <0.2 to $5 \text{ mg}/\text{m}^3$. The respirator test chamber samples have had DOP concentrations ranging from 15 to $80 \text{ mg}/\text{m}^3$.

INFRARED SPECTROSCOPY

TRIBUTYL PHOSPHATE IN AQUEOUS NITRIC-ACID WASH SOLUTIONS

Patricia A. Hyman and Roger S. Cichorz

Summary:

The concentration of trace quantities of tributyl phosphate (TBP) in aqueous nitric-acid wash solutions can be rapidly determined by extracting the sample with carbon tetrachloride (CCl_4) and quantitatively measuring, by infrared spectroscopy, the alkyl (C-H) absorption of TBP in the CCl_4 extract.

Experimental:

The TBP is soluble in water only to the extent of 1 millilitre (ml) TBP per 165 ml water. It is more soluble in nonpolar organic solvents; thus CCl_4 quantitatively extracts TBP from an aqueous solution. This method is valid only when TBP is the sole C-H absorber in the aqueous wash solutions. Standard solutions of TBP in CCl_4 in the concentration range of 50 to 3000 parts per million by volume (ppm) were prepared, and the C-H infrared absorbance at 3.4 micrometres (μm) for each standard was measured by the baseline method.

The standards were contained in a 10-centimetre path-length glass cell with sodium chloride windows, and the C-H absorbance was measured differentially against CCl_4 contained in a matched reference cell. A Beer-Lambert plot of absorbance at $3.4 \mu\text{m}$ versus concentration of TBP in CCl_4 was linear over the concentration range of 50 to 3000 ppm. A typical Beer-Lambert plot is given in Figure 3.

Standard aqueous solutions of TBP in the concentration range of 100 to 500 ppm were also prepared. A one-to-one by volume extraction with CCl_4 was performed on each, and the C-H absorbance measured. The concentration of TBP in each aqueous standard solution was calculated using the standard Beer-Lambert plot and was compared to the actual concentration of the aqueous TBP

FIGURE 3. Beer-Lambert Calibration Plot Based on the 3.4 Micrometre Alkyl Absorbance of Tributyl Phosphate in Carbon Tetrachloride.

TABLE IV. Recoveries of Tributyl Phosphate from Aqueous Solutions.

Actual Concentration of Aqueous Standard (parts per million by volume)	Calculated Mean Recovery	Percent Recovery
100	99	99.0
250	237	94.8
500	542	108.4
		Mean = 100.7
		Standard Deviation = 7.0

standard. The mean percent recovery was found to be 100.7 percent (± 13.7) at the 95-percent confidence level. Recovery data are given in Table IV. The reproducibility of the standard determinations was ± 15 percent.

DETERMINATION OF PHOSPHATE ESTER IN METHANOL

Patricia A. Hyman

Summary:

Using infrared spectroscopy, it is possible to indirectly measure the volume percent dihexyl-diethylcarbamylmethylene phosphate (DHDECMP) in methanol solutions. Methanol has an intense infrared spectrum which obscures that of DHDECMP when the two substances are present in a mixture; thus it is first necessary to separate the methanol from the DHDECMP via evaporation (DHDECMP is not volatile). The DHDECMP residue is then quantitatively dissolved in carbon tetrachloride (CCl_4) and volume percent DHDECMP is determined by measuring either the alkyl (C-H) absorbance or the carbonyl (C=O) absorbance of the DHDECMP.

Experimental:

Standard solutions of DHDECMP in methanol in the concentration range of 0.02 to 1.0 volume percent were prepared. The methanol was evaporated from a known volume of each standard and the DHDECMP residue was quantitatively transferred with CCl_4 to a 10-centimetre path-length glass cell with sodium chloride windows. The C-H absorbance at 3.4 micrometres (μm) and the C=O absorbance at 5.7 μm were measured differentially against CCl_4 in a matched reference cell using the baseline method. Standard Beer-Lambert plots of absorbance at 3.4 μm or absorbance at 5.7 μm versus percent DHDECMP in the standard methanol solution were prepared and were found to be linear over the following concentration ranges:

For wavelength = 3.4 μm ; linear concentration range = 0.02 to 0.3 percent

For wavelength = 5.7 μm ; linear concentration range = 0.10 to 1.0 percent

Typical Beer-Lambert plots are given in Figure 4. The great difference in intensities of the absorbances

FIGURE 4. Beer-Lambert Calibration Plots for Dihexyldiethylcarbamylmethylene Phosphate (DHDECMP) in Methanol.

at 3.4 and 5.7 μm allows for the application of this method over a wide concentration range. The reproducibility of the standard determinations is ± 15 percent. No recovery factor is needed for this method since the samples are analyzed in exactly the same manner as the standards.

ANALYSIS OF CARBON TETRACHLORIDE SOLUTIONS FOR PHOSPHATE ESTER

Patricia A. Hyman

Summary:

The concentration of dihexyldiethylcarbamylmethylene phosphate (DHDECMP) in an unknown

DHDECMP-carbon tetrachloride (CCl_4) mixture can be rapidly determined using infrared spectroscopy. The volume percent of DHDECMP is determined by measuring the infrared absorption maximum at 7.2 micrometres (μm) of either the sample mixture or an appropriate quantitative dilution.

Experimental:

The DHDECMP- CCl_4 standard mixtures were prepared in the concentration range of 1.00 to 10.0 volume percent DHDECMP, and the infrared absorption at 7.2 μm of each standard was measured by the baseline method. The standards were contained in a sodium chloride cavity cell with a fixed path length of 0.10 millimetres, and the absorption at 7.2 μm was measured against air. A Beer-Lambert plot of absorbance at 7.2 μm versus percent DHDECMP was linear over the concentration range of 1 to 10 percent. The reproducibility of the standard determinations was ± 10 percent. No recovery factor is necessary as the samples are analyzed in the same manner as the standards. An appropriate factor is required if the sample were quantitatively diluted before placing it in the cell.

AQUEOUS NITRIC-ACID WASH SOLUTIONS FOR PHOSPHATE ESTER

Patricia A. Hyman

Summary:

The concentration of trace amounts of dihexyldiethylcarbamylmethylene phosphate (DHDECMP) in aqueous nitric-acid wash solutions can be determined by extracting the sample with carbon tetrachloride (CCl_4) and quantitatively measuring the C-H absorption of DHDECMP in the CCl_4 extract by infrared spectroscopy. The DHDECMP is only slightly soluble in water. It is more soluble in nonpolar organic solvents; thus CCl_4 quantitatively extracts the DHDECMP from an aqueous solution. This method is valid only when DHDECMP is the sole C-H absorber in the aqueous nitric acid solutions.

FIGURE 5. Beer-Lambert Calibration Plot for Dihexyldiethylcarbamylmethylene Phosphate (DHDECMP) in Carbon Tetrachloride.

The standards were contained in a 10-centimetre path-length glass cell with sodium chloride windows, and the C-H absorbances were measured differentially against CCl_4 contained in a matched reference cell. A Beer-Lambert plot of absorbance at $3.4 \mu\text{m}$ versus concentration of DHDECMP in CCl_4 was linear over the concentration range of 50 to 1000 ppm. A typical Beer-Lambert plot is given in Figure 5.

Standard aqueous solutions of DHDECMP in the concentration range of 100 to 500 ppm were also prepared. A one-to-one by volume extraction with CCl_4 was performed on each, and the C-H absorbance was measured. The concentration of DHDECMP in each aqueous standard solution was determined from the standard Beer-Lambert plot and compared to the actual concentration of the aqueous DHDECMP standard. The mean percent recovery was found to be 97 percent (± 41) at the 95-percent confidence level. Recovery data are given in Table V. The reproducibility of the standard determinations was ± 15 percent.

TABLE V. Recoveries of Phosphate Ester from Aqueous Solutions.

Actual Concentration of Aqueous Standard (parts per million by volume)	Calculated Mean Recovery	Mean Percent Recovery
100	121	121
250	228	91
500	399	80
	Mean = 97	
	Standard Deviation = 21	

SAMPLING METHODS

HEADSPACE GAS SAMPLING OF VIALS CONTAINING PLUTONIUM-CONTAMINATED MATTER

Duane I. Hunter and Tom L. McFeeters

Summary:

A method has been developed to extract non-contaminated gas samples from sample vials containing plutonium-contaminated matter. The method can be used on any type or size of vial, providing the vial is sealed with a flexible plastic cap which can be pierced with a hypodermic needle.

Experimental:

A hypodermic needle is attached to a vacuum manifold inside a glove box. The pumping system

Experimental:

Standard solutions of DHDECMP in CCl_4 in the concentration range of 50 to 1000 parts per million by volume (ppm) were prepared, and the C-H absorbance at $3.4 \mu\text{m}$ for each standard was measured by the baseline method.

FIGURE 6. Schematic Representation of the Gas Sampling Manifold.

FIGURE 7. Needle and Septum Positioning during Evacuation and Sampling.

outside of the glove box is protected from contamination by 0.3-micron particulate filters. The vacuum manifold passes through the glove-box wall to a 0.3-micron filter. A noncontaminated 10-cubic centimetre sample container connects to the exterior of the filter (Figure 6).

A gas chromatographic septum placed on the end of the hypodermic needle seals the hole (Figure 7). The complete system is then evacuated to less than

0.1 torr (13.3 pascals). The valve to the pump is then closed, and the sample vial is pushed onto the needle. The septum acts as a seal between the needle and vial as the needle punctures the vial cap. The headspace gas can then expand through the filter and into the sample bottle.

The headspace volume in the vial can be determined. The previously sampled vial is allowed to equilibrate with the known glove-box pressure while still on the needle. The manifold is evacuated and the pump valve closed. The known pressure in the vial is then expanded into a known volume and the new pressure is recorded. Using the ideal gas law and knowing the temperatures, the original vial volume can be calculated.

Experimental trials involving pure helium inside the sample vial have produced samples for analysis that contain greater than 85-volume percent helium; that is, introduction of laboratory atmosphere into the actual sample appears relatively minimal. Gas samples obtained employing this procedure have contained no radioactive contamination and can be directly transferred without any further precautions to a suitable instrument for analysis (e.g., a mass spectrometer or gas chromatograph).

METHOD FOR OBTAINING HEADSPACE GAS SAMPLES FROM SEALED PRODUCE CANS

*Tom L. McFeeters, Duane I. Hunter,
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Summary:

Headspace gas in sealed produce cans, including those containing large quantities of radioactive material, has previously been sampled by two methods. The first method was direct sampling with a vacuum bottle equipped with a 0.125-inch steel-tubing needle. Results from this method were semiquantitative with unknown minimum detectable limits.

The second method involved placing the complete can inside of a heavy-walled steel container. This

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FIGURE 8. Sampling Manifold.

gave protection from potentially explosive cans. The extra volume of the outer container increases the lower detectable limits. The heavy container limited the portability and required a separate fixture for each can size.

The headspace sampler described here was designed to provide a portable unit capable of accurate quantitative analysis while limiting the spread of radioactive contamination to the sample or the outer can surface. The lower detectable limit was reduced to that of the instrument used for the gas analysis (mass spectrometer or gas chromatograph) and was not increased by the sampling procedure.

Experimental:

The headspace sampling hardware consists of two main sections, the sampling manifold (Figure 8)

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FIGURE 9. Sealing Hardware.

and the sealing hardware (Figure 9). The sampling manifold consists of a 0.125 inch stainless steel needle connected through a 2-micrometre sintered stainless-steel filter to a pressure gauge, vacuum pump, and sample bottle. The sealing hardware has a 0.125-inch Veeco® fitting welded to a 5-centimetre disk. A 2-millimetre thick neoprene gasket was used to seal the disk to the can. A bracket on the top and the bottom of the can was used to hold the disk fitting in place.

To sample the headspace, the needle is inserted into the Veeco fitting but not through the neoprene gasket. The complete manifold is then evacuated and checked for leaks by closing the vacuum valve and monitoring for an increase in pressure. The gas sample is collected by forcing the needle through the gasket and the can top, and expanding the gas into the sample bottle (Figure 10). The sample bottle is closed, removed from the manifold, and transferred to the mass spectrometer for gas analysis.

FIGURE 10. Headspace Sampling Assembly Activated for Sampling.

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The can headspace volume and original headspace pressure may be determined by removing the original sample bottle and allowing the pressure to equilibrate through the filter with a known-line pressure. A second known volume replaces the sample bottle and the gas is expanded into the evacuated volume. Using the ideal gas law, and the original pressure and volume, each gas in the sealed container can be calculated.

The main outer can surface can be kept free of contamination by careful removal of the punch manifold and sealing hardware. The small hole in the can top can be covered with tape or black wax. Any contaminated portion of the hardware (needle, filter, gasket, and Veeco fitting) may be replaced before another analysis.

MISCELLANEOUS PROJECT

DISTILLATION AND REUSE OF CHLOROFORM WASTE

Reuben J. Sironen

Summary:

The accumulation of relatively large volumes (3 to 4 litres daily) of the chloroform extract of the gallium (Ga)-oxine complex produced during spectrophotometric Ga determinations has caused problems of storage, shipping, and disposal. Furthermore, the carcinogenic nature of the chloroform solvent suggests that it be handled only in well-ventilated hoods or glove boxes. Distillation and reuse of the chloroform wastes offer a solution to these concerns.

Experimental:

Distillation of the chloroform waste yielded a distillate which is acceptable for reuse in the Ga

method, provided the waste is prescrubbed with aqueous one-percent sodium hydroxide. The scrubbing step is necessary to remove acetic acid and methanol impurities identified by infrared spectroscopy in the chloroform distillate which had not been prescrubbed. Gallium concentration in the distillate approximates that of reagent-grade chloroform.

Using a single conventional distillation setup of Pyrex® glass, 4 litres of chloroform waste can be distilled daily with approximately 65 percent recovery. The remainder is lost through evaporation at the outlet of the condenser. The straight-tube water-jacket condenser will be replaced soon with a coil-tube condenser for greater efficiency. At the present time, cooling water is continuously recirculated from a 4-litre reservoir and reaches a temperature of about 47 °C while chloroform distills at about 55 °C at this altitude. A better system of cooling the vapors may be devised in the future. After collecting four litres of distillate, a portion is submitted for infrared spectroscopic analysis, and another portion is reserved for a blank determination by the Ga-oxine method. If the infrared spectroscopy analysis results indicate minimum concentrations of impurities and the blank readings are sufficiently low, the distilled chloroform is stabilized by adding 0.75-volume percent methanol and is ready for use in spectrophotometric Ga determinations.

Because of physical space considerations, it is not possible to distill the chloroform in the same glove box in which the Ga samples are prepared. Consequently, the glove box in which the distillations are performed is about 15 feet from the Ga glove box. To avoid transferring bottles of waste and distillate between boxes, overhead lines of stainless steel have been installed permitting the back-and-forth transfer of the liquids by air pressure. In this manner, the distilled chloroform goes directly to the buret for delivery to the Ga extraction vessel. This arrangement also permits introduction of new chloroform solvent as needed to make up for evaporation losses without the hazard of exposing laboratory personnel to vapors while transferring chloroform to a buret reservoir outside the glove box.