LA-3452

c. 3

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

The Determination of Nitride Nitrogen in Plutonium Metal, Alloys, and Compounds

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

Printed in USA. Price $1.00. Available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, United States Department of Commerce, Springfield, Virginia

LA-3452
UC-4, *CHEMISTRY*
TID-4500

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

Report written: January 14, 1966

Report distributed: March 1, 1966

The Determination of Nitride Nitrogen in Plutonium Metal, Alloys, and Compounds

by

E. A. Hakkila
G. R. Waterbury

ABSTRACT

Nitride nitrogen in plutonium metal, alloys, or compounds is separated by steam distillation as ammonia, trapped in a boric acid solution, and measured either spectrophotometrically using Nessler's reagent or by titration with standardized acid, depending upon the quantity of nitrogen present. The samples are dissolved and digested in a mixture of hydrochloric and perchloric acids, and the solutions are made strongly alkaline prior to the steam distillation. For the spectrophotometric measurement, the color-forming reagent is added to the boric acid solution, and the absorbance is measured at a wavelength of 410 mμ. The molar absorptivity of the colored species is 3500. The standard deviations in measuring 1 to 100 μg. of nitrogen spectrophotometrically in 1-gram samples range from 30 to 3%. For the titrimetric measurement, the boric acid solution containing the ammonia is titrated directly with dilute standardized hydrochloric acid. The relative standard deviations of the titration method in measuring 100 to 2000 μg. of nitrogen are in the range from 6 to 0.7%. Results for nitrogen in plutonium metals obtained by the spectrophotometric method are essentially equal to the values obtained by a Dumas method, indicating that the nitrogen exists predominantly in the combined or nitride form.

ACKNOWLEDGMENTS

The authors acknowledge the assistance of C. F. Metz under whose supervision this work was performed. The authors are indebted to H. J. Kavanaugh for mechanical cleaning of the plutonium specimens, and to Helen L. Barker for obtaining much of the data.

INTRODUCTION

The conversion of nitride nitrogen to ammonium salts upon acid dissolution of plutonium has been reported to occur.(2) The subsequent treatment in the case of plutonium metal or alloys, as with most others, involves a steam distillation after making the solution strongly basic. The completeness of the recovery of evolved ammonia from ammonium salts present with the hydrolyzed metals in this step is easily tested and has been found to be satisfactory with plutonium (as it is known to be with many other materials). Winkler's technique of trapping the ammonia in boric acid solution is used, and the ammonia is measured either by titration with standard acid or spectrophotometrically following reaction with Nessler's reagent. The latter is more convenient for low levels of nitrogen. Nessler's reagent contains $(HgI_4)^{-2}$ which reacts with traces of ammonia to form an insoluble yellow to orange-red compound, $HgI_2 \cdot HgNH_2I$. In the presence of a stabilizer such as gum arabic, a highly dispersed colloidal system is formed which responds as a true colored "solution" in spectrophotometry. The ever-present traces of ammonium salts and ammonia about the chemical laboratory must be very carefully excluded from all reagents and glassware when analyzing samples containing microgram quantities of nitrogen. Aldehydes, acetone, and alcohols interfere with the development of the color with Nessler's reagent(1) and must be removed from samples prior to analysis.

SAMPLE PREPARATION

Samples of plutonium metal are received for nitrogen analysis in the form of large chunks. For samples contaminated with cutting oil, the piece is washed with methyl chloroform and dried at room temperature before sampling. Then the piece is carefully polished with a file or emery paper, and cut with sidecutters or a chisel into approximately 1-gram pieces for analysis. Samples should be dissolved as soon as possible after weighing to minimize nitride contamination of the surface. Samples stored in alcohol or cleaned with acetone must be thoroughly dried before dissolution of the sample. The operations of cleaning, cutting, and weighing should be done in an inert atmosphere enclosure if suitable facilities are available. In that case, the cleaned pieces are placed in vials in the enclosure for the transfer to the analysis equipment. Then the vial is opened, and the sample is dropped quickly into the acid solution for dissolution.

APPARATUS AND REAGENTS

Apparatus

Bottles, narrow-mouth, amber, 500-ml.

Bottles, polyethylene, 16-oz.

Digestion apparatus, consisting of a round-bottom, short-neck, 50-ml. distilling flask fitted to a water-cooled condenser with a 24/40 standard taper joint; a 115-v., 2.5-in.-diameter electric heating mantle; and a variable transformer for controlling the temperature of the mantle. The temperature should be adjusted to cause refluxing of the acid during the digestion.

Heating mantle, 115-v., Glas-Col, approximately 5-in. in diameter, with support clamp and a 5-amp. variable transformer for adjusting voltage, for heating steam generator flask.

Normal laboratory glassware, including pipets, volumetric flasks, beakers, etc.

Spectrophotometer, Beckman model DU with matched cells having 1-cm. light paths.

Steam distillation apparatus, as shown in Figure 1.

Variable transformer, 5-amp., 115-v.

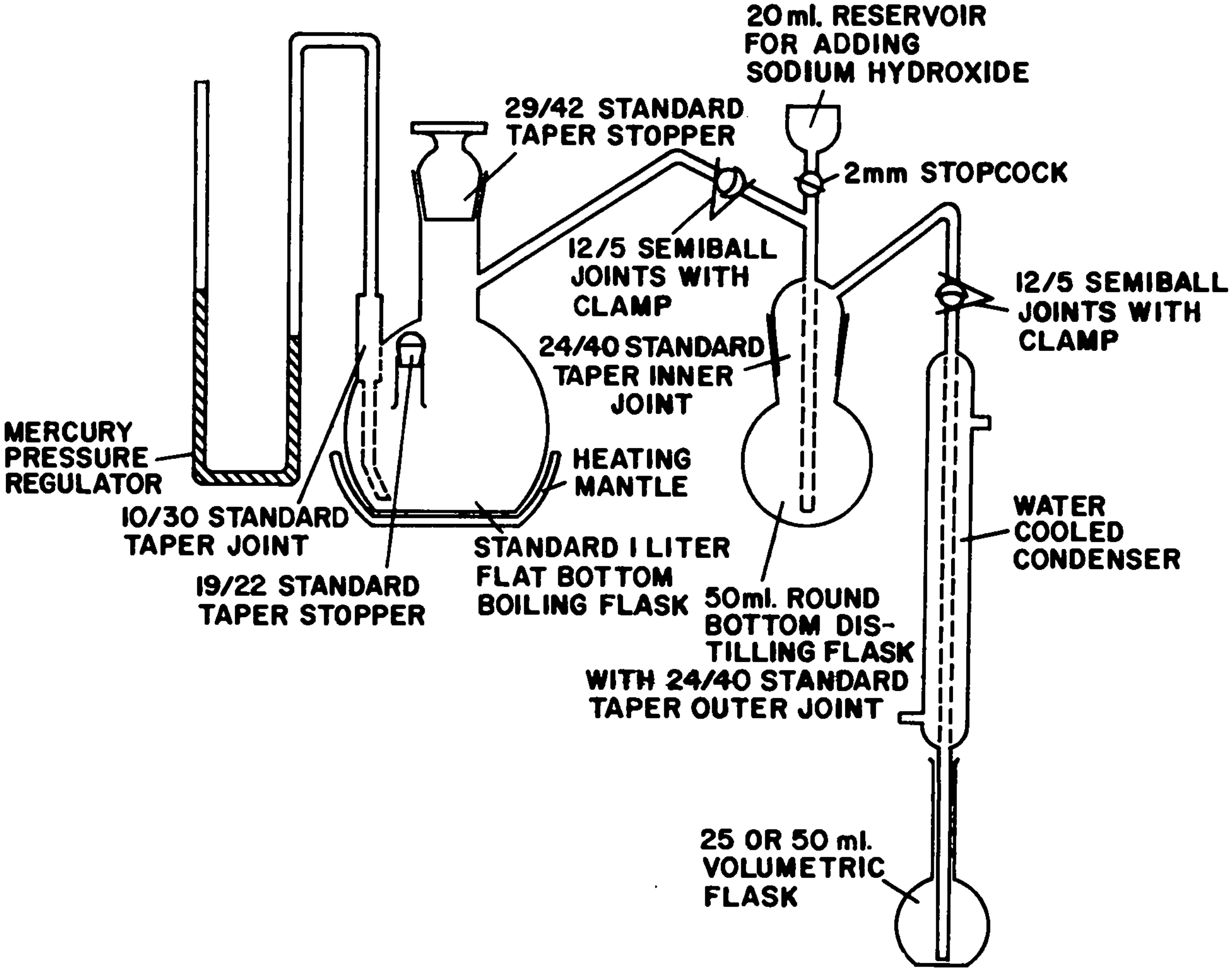

Figure 1. Steam distillation apparatus.

Reagents

Ammonium chloride, reagent grade.

Anion exchange resin, Dowex-50, 200- to 400-mesh. Wash the resin with several portions of 6 M hydrochloric acid until the washings are clear. Then wash with ammonia-free distilled water until the pH of the washings is greater than 4.

Boric acid, 5%. Dissolve 5 grams of reagent grade boric acid in 95 ml. of ammonia-free distilled water.

Gum Arabic, USP.

Hydrochloric acid, reagent grade, 38%.

Hydrochloric acid, 6 M. Dilute 500 ml. of 38% hydrochloric acid to 1 liter with distilled water.

Hydrochloric acid, 0.02 M. Dilute about 3 ml. of 6 M hydrochloric acid to 1 liter with distilled water. Standardize this solution by titrating known quantities of primary standard sodium carbonate with this dilute acid.

Mercuric chloride, reagent grade.

Nessler's reagent. Dissolve 50 grams of reagent grade potassium iodide in 35 ml. of distilled water. Add slowly, with stirring, a saturated solution of mercuric chloride until the first slight precipitate of red mercuric iodide persists. Add 400 ml. of clear 9 N sodium hydroxide; dilute to 1 liter with ammonia-free distilled water. Allow to stand until clear and decant the clear liquid for use.

Nessler's reagent stabilizer. Dissolve 20 grams of gum arabic in 400 ml. of hot water, cool, and add 20 grams of 200- to 400-mesh Dowex-50 resin. Allow to settle and decant. Add 20 ml. of Nessler's reagent to the decanted solution, let settle for 72 hr., and decant. Store the solution in an amber bottle.

Nitrogen standard solution, 1000 and 10 μg. of nitrogen per ml. Dissolve 3.819 grams of reagent grade ammonium chloride in distilled water and dilute to 1 liter with distilled water to prepare a solution containing 1000 μg. of nitrogen per ml. Standardize by distilling the ammonia from 1-ml. aliquots into boric acid solution and titrating the ammonia with the standardized 0.02 M hydrochloric acid solution. Dilute 10.00 ml. of the standard ammonium chloride solution to 1 liter with ammonia-free distilled water to prepare a solution containing 10 μg. of nitrogen per ml.

Perchloric acid, 72%, reagent grade.

Potassium iodide, reagent grade.

Sodium carbonate, primary reagent grade, National Bureau of Standards. Dry at 275° C for 1 hr. and cool in a desiccator.

Sodium hydroxide, 9 N. Dissolve 360 grams of reagent grade sodium hydroxide pellets in distilled water and dilute to 1 liter.

Sodium hydroxide, 50%. Dissolve 200 grams of reagent grade sodium hydroxide pellets in 200 ml. of distilled water and stir vigorously until dissolved. Cool to room temperature and store in a polyethylene bottle.

Water, distilled, ammonia-free. Triple-distilled water is sufficiently pure, or water may be distilled from a very dilute sulfuric acid solution.

RECOMMENDED PROCEDURE

The weighed, 1-gram piece of polished plutonium is placed in a short-neck, 50-ml. round-bottom flask, and 5 ml. of 38% hydrochloric acid are added to dissolve the metal. When the reaction ceases, 2 ml. of 72% perchloric acid are added, the flask is clamped in place in the heating mantle on the digestion stand, and the condenser is attached to the flask. The sample is digested for 30 min. and allowed to cool to room temperature, and approximately 10 to 20 ml. of triple-distilled water are added.

The flask is clamped in place on the distillation apparatus which is assembled making sure all connections are tight. The heating mantle on the steam generator is turned on, but the flask is not stoppered. A 50-ml. volumetric flask containing 2 ml. of 5% boric acid and 15 to 25 ml. of triple-distilled water is placed under the condenser so that the condenser tip extends below the surface of the liquid. If the sample is known to contain less than 20 ppm of nitrogen, a 25-ml. flask containing 2 ml. of boric acid solution and 5 to 10 ml. of triple-distilled water is used. Fifteen ml. of 50% sodium hydroxide are added to the funnel in the distillation head, and the sodium hydroxide is allowed to run slowly into the acid plutonium solution. If there is any tendency for the sodium hydroxide to be forced up the side arm to the steam generator, the stopper is placed momentarily on the steam generator. When the sodium hydroxide has been forced out of the side arm, the stopper is removed, and the addition of sodium hydroxide continued. Immediately following addition of the sodium hydroxide, the funnel stopcock is closed, the stopper is placed on the steam generator, and the steam distillation is continued until approximately 20 ml. of distillate has collected in the 50-ml. receiving flask, or 12 ml. has collected in the 25-ml. flask. The steam generator is turned off, the clamp connecting the distillation head to the condenser removed quickly, and the stopper removed from the steam generator. The distillation flask is allowed to cool so that it may be removed for the next sample. A blank is prepared to contain 2 ml. of perchloric acid, 5 ml. of hydrochloric acid, and 10 to 20 ml. of triple-distilled water in a 50-ml. round-bottom flask. Steam distillation is carried out as described for samples.

If a 50-ml. receiver is used, the distillate is diluted to volume with triple-distilled water and shaken, and 5.00 ml. of the solution is transferred to another 50-ml. volumetric flask containing 30 to 40 ml. of triple-distilled water and 2 ml. of 5% boric acid. Both flasks are to be retained, and a full 45 ml. is to be left in the receiver flask. If the 25-ml. receiver is used, do not dilute to volume, because the color is developed using the entire distillate.

A series of solutions is prepared by pipetting 0, 1.00, 2.00, 6.00, 8.00, and 10.0 ml. of standard nitrogen solution (0, 10, 20, 60, 80, and 100 μg. of nitrogen, respectively) into separate 50-ml. volumetric flasks containing approximately 35 ml. of ammonia-free water and 2 ml. of 5% boric acid. If the 25-ml. volumetric flasks are used for samples, 0, 1.00, 2.00, and 5.00 ml. of standard nitrogen solution are pipetted into 25-ml. flasks containing 2 ml. of 5% boric acid solution and 15 ml. of distilled water. One ml. each of Nessler's stabilizer and Nessler's reagent are added carefully with volumetric pipettes to each 50-ml. flask containing either a 5-ml. aliquot of distillate from the blank solution or the sample, or the entire "known" solution. If the 25-ml. receiver flasks were used, 1.00 ml. each of Nessler's stabilizer and of Nessler's reagent are added to each 25-ml. flask. Each solution is diluted to volume with triple-distilled water and allowed to stand 10 min. The absorbance of each sample and standard solution is measured at a wavelength of 410 mμ using the solution that does not contain added nitrogen as a reference. The amount of nitrogen in each "known" solution is plotted as a function of absorbance to prepare a calibration curve. The calibration curve must be reproduced once a week; standards containing 10 or 50 μg. of nitrogen should be distilled and analyzed daily to insure the validity of the calibration curve.

The amounts of nitrogen in the distilled blank and in samples are determined using the calibration curve. The amount of nitrogen in the distilled blank is subtracted from the amount found in each sample. If the absorbance of the sample in the 5-ml. aliquot corresponds to less than 10 μg. of nitrogen, Nessler's stabilizer and reagent are added to the 45-ml. aliquot,and the absorbance is measured as described above.

The concentration of nitrogen in the sample is calculated using the equation:

$$\text{N, ppm} = \frac{\text{N found, } \mu\text{g.}}{(\text{Sample wt., grams})(\text{F})}$$

In this equation F equals 0.1 if the 5-ml. aliquot from the 50-ml. flask is analyzed, 0.9 if the 45-ml. aliquot is analyzed, or 1.0 if the entire distillate solution in the 25-ml. receiver flask is analyzed.

If the absorbance of the 5-ml. aliquot of the sample in the receiver flask corresponds to greater than 10 μg. of nitrogen, quantitatively transfer the 45-ml. aliquot to a 250-ml. Erlenmeyer flask, add 5 drops of mixed indicator, and titrate to the gray end point with the 0.02 $\underline{\text{M}}$ standardized hydrochloric acid. Calculate the concentration of nitrogen in the sample using the equation:

$$\text{N, ppm} = \frac{(\text{Volume of HCl})(N_{\text{HCl}})(0.014007)}{(\text{Sample wt., grams})(0.9)}$$

RELIABILITY

Samples of plutonium containing a known concentration of nitrogen homogeneously distributed throughout the metal were not available. Therefore, the precision of the method was determined by digesting and distilling known amounts of ammonium chloride added to aliquots of an ammonia-free plutonium solution. The relative standard deviations at various concentration levels are shown in Table I. For the distillation of 50 micrograms into 25-milliliter volumetric flasks, a negative bias of 3 percent was observed, indicating incomplete distillation using a distillation volume of 10 to 15 milliliters. Therefore, for samples containing greater than approximately 20 parts per million of nitrogen, 50-milliliter flasks are recommended as receivers and 20 milliliters of distillate are collected.

Table I

Precision of the Determination of Nitride Nitrogen in Plutonium

N present, μg.	Standard deviation, μg.		Relative standard deviation, %	
	Spectrophotometric	Titration	Spectrophotometric	Titration
0	0.33 (a)	--	--	--
1	0.29 (a)	--	30	--
2	0.44 (a)	--	20	--
7.5	0.40 (a)	--	5	--
10	1.3 (b)	--	13	--
20	2 (b)	--	10	--
50	1.5 (a)	--	3.0	--
60	2 (b)	--	3.3	--
90	3 (b)	--	3.3	--
108	--	6	--	6
529	--	4	--	0.78
1048	--	8	--	0.75
2070	--	15	--	0.72

(a) 25-ml. volumetric flasks
(b) 50-ml. volumetric flasks

Nitrogen may be present in plutonium either in the form of combined (nitride) or adsorbed nitrogen. A series of samples obtained from the same plutonium metal specimen were analyzed using the Kjeldahl and a Dumas method to determine the relative amounts of the two forms of nitrogen in plutonium. The Kjeldahl method detects only combined nitrogen. Samples were analyzed in the unpolished condition and after electropolishing in a potassium carbonate solution. Results (Table II) indicate that significant amounts of both nitride and adsorbed nitrogen are present on the surface of unpolished samples. The higher results obtained by the Dumas method on electropolished samples possibly were caused by incomplete removal of adsorbed nitrogen by the polishing procedure.

Table II

Effect of Electropolishing on Determination of Nitrogen in Plutonium

Method	No. of samples	N found, ppm
Kjeldahl, unpolished	10	37 ± 3
Dumas, unpolished	8	76 ± 27
Kjeldahl, polished	6	10 ± 3
Dumas, polished	10	27 ± 7

To further test the accuracy of the Kjeldahl method compared to the Dumas method, ten 3-gram samples were analyzed by the Kjeldahl method and six 8-gram samples were analyzed by the Dumas method. Each of these sixteen samples was mechanically polished to remove all traces of surface contamination. An average value of 9 ± 1.4 parts per million of nitrogen obtained by the Kjeldahl method, compared to 10 ± 2.5 parts per million by the Dumas method indicates that adsorbed nitrogen exists only in the oxide coating of the plutonium metal. Essentially all of the nitrogen in the polished metal is in the combined or nitride form.

Various mechanically polished plutonium alloys were analyzed by the two methods (Table III). Each value shown is the average of duplicate analyses of 1-gram samples for the Kjeldahl method and 2-gram samples for the Dumas method.

Table III

Determination of Nitrogen in Plutonium Metal and Alloys by the Kjeldahl and Dumas Procedures

Sample	ppm N, Kjeldahl	ppm N, Dumas
Pu-Fe	13 ± 3	15 ± 7
Pu-Ni	15 ± 3	28 ± 7
Pu-Fe	13 ± 3	9 ± 7
Pu-Co	8 ± 3	11 ± 7
Pu-Ce-Fe	440 ± 30	420 ± 15
Pu-Ce-Fe	60 ± 3	46 ± 7
Pu	31 ± 3	28 ± 7
Pu	20 ± 3	11 ± 7
Pu-Fe	285 ± 30	270 ± 10
Pu-Fe	10 ± 3	8 ± 7
Pu-Ce-Fe	830 ± 30	810 ± 30

Analyses indicate that nitrogen is present in freshly polished plutonium as the combined nitride form, and results obtained by the Kjeldahl method are comparable to values obtained by the more cumbersome Dumas technique. Therefore, nitrogen is determined in plutonium metal and alloys routinely by the Kjeldahl steam-distillation method in which the separated ammonia is either titrated or measured spectrophotometrically.

REFERENCES

(1) Boltz, D. F., "Colorimetric Determination of Nonmetals," p. 85, Interscience Publishers, Inc., New York, 1958.

(2) Brown, F., Ockenden, H. M., and Welch, G. A., J. Chem. Soc., (1955) 4196.