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DETERMINATION OF NITRIDE NITROGEN IN IRRADIATED MATERIALS

by

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ABSTRACT

A method for determining nitride nitrogen was adapted for analyses of irradiated samples in a hot cell. Sections of stainless steel cladding material or fuel are dissolved remotely using various combinations of H_2SO_4 , HCl , and HF . The nitrogen is separated from the highly radioactive sample solution by steam distillation using the Kjeldahl method. The collected distillates are moved from the hot cell to an open-front box where they are treated with Nessler's reagents for spectrophotometric measurement. The absorbance is measured at a 410-nm wavelength. The standard deviation for measuring 50 μg of nitrogen is $<2 \mu g$ of nitrogen using this method.

I. INTRODUCTION

The migration of nitrogen between reactor fuels and claddings during irradiation causes changes in the properties of reactor materials that are important to reactor engineers in their studies of reactor fuels and other components. For this reason, an established method for determining nitride nitrogen in plutonium metal, alloys, and compounds¹ was adapted for use in hot cells under remote conditions for analyzing irradiated materials.

In adapting this method to hot cell use, the apparatus was modified to make manipulations simpler and safer, and to achieve accurate results quickly under remote conditions. The samples are dissolved and digested remotely in acids, the solutions are made strongly basic with sodium hydroxide, and the nitrogen is steam distilled as ammonia from the solution. Winkler's technique of trapping the ammonia in a boric acid solution is used. Then the samples are removed from the hot cell and treated with Nessler's reagent in an open-front box for spectrophotometric measurement. Nessler's reagent contains $(HgI_2)^{-4}$, 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 that responds as a true colored "solution" in spectrophotometry. Care should be taken to exclude traces of ammonium salts and ammonia from all reagents and glassware when analyzing microgram quantities of nitrogen. Aldehydes, acetone, and alcohols interfere with the development of the color with Nessler's reagent.

II. SAMPLE PREPARATION

Irradiated materials are received in the hot cell for nitrogen analysis in the form of 6- to 12-mm-long sections of fuel pellets or claddings. Fuel pellets are weighed and stored in vials until dissolved using the sealed-reflux dissolution system.² Cladding samples are cut remotely with end-cutting pliers into pieces of approximately 100 mg each, which are cleaned in warm 15M HNO₃ acid for 1 h or a 6M HCl solution at room temperature for 1 min. In either case, samples must be rinsed thoroughly with double-distilled water and then dried in labeled vials on a hot plate, weighed, and stored until dissolution.

III. APPARATUS AND REAGENTS

A. Apparatus

Balance, analytical, capable of weighing to ± 0.0001 g.

Bottles, glass, narrow-mouth, amber, 500-mL, and polyethylene, 500-mL and 125-mL.

Dissolution apparatus, consisting of a 125-mL distillation flask (Fig. 1) covered with a 50-mm watch glass and a 115-V hot plate wired to a variable transformer located outside the cell to regulate temperature.

For dissolving (U,Pu)O₂ samples, a borosilicate or a fused silica sealed-reflux tube with rubber or polyethylene stopper and a No. 18 pinch clamp as shown in Fig. 2 and described in LA-5776² is used.

Hot plate, 115-V autemp-type, with a heating surface approximately 7.5 cm (3 in.) in diameter controlled by a variable transformer outside the cell to adjust temperature for heating steam generator flask.

Normal laboratory glassware, including pipets, volumetric flask, and beakers.

Spectrophotometer, Bausch and Lomb Spectronic 100 or equivalent, with 1-cm cells.

Steam distillation apparatus, 1000-mL steam generator, distillation head, 125-mL distillation flask, and condensor tube as shown in Figs. 3 and 4.

B. Reagents

Ammonium chloride, analytical reagent grade.

Anion exchange resin, Dowex 50 W-X4, 200- to 400-mesh resin. Wash the resin with several portions of 6M HCl until the washings are clear. Then wash with double-distilled water until the pH of the washings is greater than four.

Boric acid, 5%. Dissolve 5 g of reagent-grade boric acid in 95 mL of double-distilled water.

Gum arabic, USP.

Fig. 1.
Dissolution-distilling flask.

Fig. 2.
Sealed-reflux tube.

Hydrochloric acid, analytical reagent grade 12M.

Hydrochloric acid, 6M. One part by volume of 12 M HCl with one part by volume of double-distilled water.

Hydrofluoric acid, analytical reagent grade, 27M.

Sulfuric acid, analytical reagent grade, 18M.

Mercuric chloride, analytic reagent grade.

Steel standard reference material, NBS-8i (180 ppm N).

Nessler's reagent. Dissolve 50 g of reagent-grade potassium iodide in 35 ml of water. Add slowly, while stirring, a saturated solution of mercuric chloride until the first slight precipitate of red mercuric iodide persists. Add 400 ml of clear 9M sodium hydroxide; dilute to 1 l with

Fig. 3.
Distillation apparatus.

ammonia-free distilled water. Allow to stand until clear (usually 1 h) and decant the clear liquid for use.

Nessler's reagent stabilizer. Dissolve 20 g of gum arabic in 400 ml of hot water, cool, and add 20 g 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 h, and decant. Store the solution in an amber bottle.

Nitrogen standard solutions, 1.00 and 0.010 mg nitrogen per ml. Prepare a solution to contain 1.00 mg of nitrogen per ml by dissolving 3.819 g of reagent-grade ammonium chloride in ammonia-free double-distilled water and dilute to 1 l with double-distilled water. Standardize by distilling 1.00 ml aliquots into boric acid and titrating the distilled ammonia with standardized, approximately 0.02 M hydrochloric acid solution. To prepare a solution to contain 0.010 mg of nitrogen per ml, dilute 10 ml of the standard ammonium chloride to 1 l with double-distilled water.

Potassium iodide, analytical reagent grade.

Sodium hydroxide, 9M. Dissolve 360 g of analytical reagent-grade sodium hydroxide pellets in double-distilled water and dilute to 1 l.

Sodium hydroxide, analytical reagent-grade, 50% solution.

Water, distilled, ammonia-free, or double-distilled (D.D.) water is sufficiently pure.

Fig. 4.
Detail of distilling head and distilling flask.

IV. RECOMMENDED PROCEDURE

CAUTION. Health-safety rules for handling plutonium must be followed rigidly, and adequate protection for the operator must be ensured by use of suitable glove boxes and protective clothing.

In dissolving clad samples, the weighed sample is placed in a cleaned 125-ml distillation flask and 1 ml of 18M sulfuric acid and 2 to 3 ml of double-distilled water are added. The flask is covered with a watch glass and the solution is heated on a hot plate at about 80°C for 1 h. Plutonium carbide and nitride fuels are placed in dissolution flasks with 5 to 7 ml of 12M HCl and heated for 1 h at 80°C. Samples are allowed to cool to room temperature, and 10 to 20 ml of D.D. water are added before the sample flask is clamped to the distillation head. Uranium-plutonium oxide fuels are dissolved by the sealed reflux method² with 5 ml of 12 M HCl containing 5 drops of 1.3 M HF. The tube is heated to 150°C and allowed to reflux for 12 to 16 h. The dissolved sample is rinsed carefully into a 125-ml distillation flask using approximately 15 ml D.D. water. For plutonium oxide (up to 1 g), 350 to 450 mg of lead is added to the sealed-reflux tube to

prevent oxidation of the nitrogen. A blank solution is prepared containing the same reagents as used to dissolve the sample.

The steam generator is filled with D.D. water, heated to boil the water, and approximately 20 mL of water is distilled to clean the system. The distillation head and condenser are disconnected and rinsed and the steam generator is left unstoppered.

The steam generator (with stopper removed), the distillation flask, distillation head, and condenser are connected together. A 50-mL volumetric flask containing 2 mL of 5% boric acid and 10 to 20 mL of D.D. water are placed under the condenser so that the tip of the condenser extends below the surface of the liquid. To the reservoir in the distillation head are added 15 mL of 50% NaOH, and by opening the stopcock, the NaOH solution is allowed to flow into the 125-mL distillation flask. If there is any tendency for the NaOH solution to be forced out the side arm to the steam generator, the stopper is placed momentarily on the steam generator. When the NaOH solution has been forced out of the side arm, the stopper is removed, and the addition of NaOH solution continued. Immediately following addition of the NaOH solution, the reservoir 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 volumetric flask. The steam generator is turned off by removing the stopper, and the clamp connecting the distillation head to the condenser is removed carefully. The distillation flask is removed and the head is rinsed with water to prepare it for the next run. Samples, standards, and blanks are distilled as described above. The distilled nitrogen samples are removed from the hot cell and taken to an open-front dry box.

A reference solution is prepared with 2 mL of 5% boric acid and approximately 45 mL of D.D. water in a 50-mL volumetric flask. One milliliter each of Nessler's stabilizer and Nessler's reagent is added to the reference solution, distilled blanks, standards, and samples. The solutions are diluted to volume, mixed, and allowed to stand for 10 min. The spectrophotometer is zeroed with the reference solution to correct for the reagents added to all the samples. The absorbance of each solution is then measured at 410-nm wavelength and the average of the two blanks is subtracted from all measurements. The nitrogen contents are calculated based on the micrograms of nitrogen per absorbance derived from an average of the two 50-μg standards of nitrogen. Calculation is as follows.

$$N, \text{ ppm} = \frac{(\text{Corrected abs of sample})(\mu\text{g/abs of std})}{\text{Sample weight}}$$

Normally, a set of analyses will include two blanks, two working standards containing 50 μg of nitrogen, and the distillates of the irradiated samples.

V. RELIABILITY

The reliability of the method was determined by distilling, under remote conditions in a hot cell, a series of steel standard reference materials, NBS-8i, having a known (180-ppm) content of nitrogen. The standards were also run with the irradiated samples for 53 days and are included in the calculations for method precision. A total of 30 determinations of nitrogen in 250-mg portions of the standard reference material was used for determining the precision of the method, along with 23 determinations of nitrogen in a standard NH_4Cl solution (see Table I).

To test the method for analyzing irradiated materials, a cross section of samples having burn-ups from 0.4 to 7.4% was chosen, and several cuts in each fuel and clad sample were prepared as

TABLE I
PRECISION DATA FOR HOT CELL APPLICATION OF
DETERMINATION OF NITRIDE NITROGEN

<u>Reference Material</u>	<u>Number of Determinations</u>	<u>Average N Found</u>	<u>SD</u>	<u>RSD</u>
NBS-8i (180 ppm N)	30	180 ppm	4.3 ppm	2.4%
50 μ g nitrogen from NH ₄ Cl working stds	23	50 μ g	1.08 μ g	2.16%

described in Sec. IV. Table II shows results of nitrogen found in fuels and the corresponding clads along with the respective atom per cent burnup of each sample.

TABLE II
NITROGEN ANALYSIS OF IRRADIATED FUEL AND CLAD

<u>Pin No.</u>	<u>Section No.</u>	<u>Nitrogen (ppm)</u>		<u>Average Nitrogen (ppm)</u>		<u>Burnup (%)</u>
		<u>Clad</u>	<u>Fuel</u>	<u>Clad</u>	<u>Fuel</u>	
1	A	450	5			
	B	490	---	470	5	2.6
2	A	440	8			
	B	440	9			
	C	390	8	420	8	0.4
3	A	320	11	320	11	7.4
4	A	740	18			
	B	680	14			
	C	680	---	700	16	4.4
5	A	680	8			
	B	570	7			
	C	590	9			
	D	760	8			
	E	730	11	670	9	0.4

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