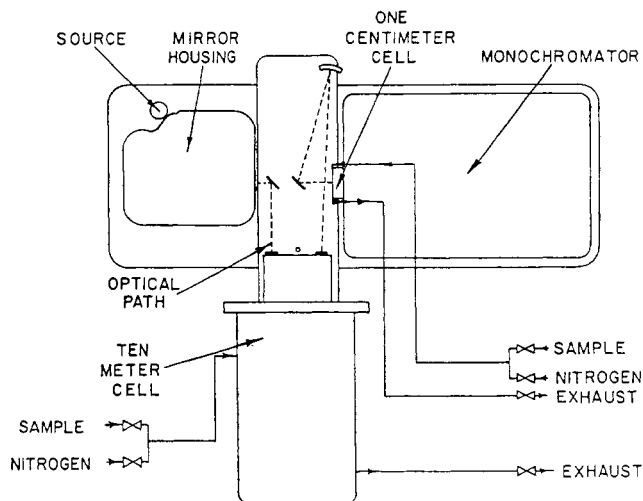


The valves are arranged so that either cell can be flushed with dry nitrogen while the appropriate sample passes through the other cell. The intensity of the infrared absorption band (at constant wave length) indicates the concentration of the component and is recorded on the strip chart of the instrument. Background absorption is determined at the analytical wave lengths with nitrogen flowing through both cells. The usual precautions must be taken when a gas is polar and may be adsorbed on the walls of the larger cell.

The flexibility of this technique makes it widely applicable to multiple component analysis. The entire operation can be made automatic by using suitable timers and valves.



Determination of Nitrogen in Uranium Nitrides

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RECENTLY, interest was shown in determining nitrogen in UN and U_2N_3 . A search of the literature revealed only a note (5) on the use of a modified Dumas technique, in which the sample is burned with exactly the right amount of potassium chlorate to give satisfactory results. This seems to indicate that a balance of errors might be operative, as a small excess of chlorate gave high nitrogen values while slightly less than optimum amounts gave low results.

Therefore, it was decided to investigate various modifications of the Kjeldahl procedure. Several digestion methods were tried, using in all cases a sample weight of approximately 100 mg.

Method 1. The sample was fumed with concentrated sulfuric acid. Potassium sulfate, copper selenate, and 30% hydrogen peroxide were added, alone and in combination. All these variations gave low nitrogen recovery on both UN and U_2N_3 .

Method 2. The sample was heated with 1 to 1 hydrochloric acid. Various amounts of hydrofluosilicic acid, hydrofluoric acid, and 30% hydrogen peroxide

were added. Using 25 ml. of 1 to 1 hydrochloric acid, 1 ml. each of hydrofluoric and hydrofluosilicic acids, and 4 ml. of 30% hydrogen peroxide gave acceptable results for UN, but low values for U_2N_3 .

Method 3. This was the Friedrich method (6), which gave acceptable results for UN. Nitrogen recovery on U_2N_3 was more nearly complete than the previous methods, but still lower than the theoretical value.

Recommended Method. The digestion mixture consisted of 1 to 1 hydrochloric acid with additions of copper selenate and hydrofluosilicic acid. Acceptable results were obtained on both UN and U_2N_3 .

APPARATUS AND REAGENTS

DISTILLATION APPARATUS. The Parnas-Wagner (4) type was modified by addition of an electrically heated steam generator consisting of a 2-liter reaction vessel with immersion heater, and a three-way stopcock placed between steam generator and still. This allows the steam to be exhausted to the drain and the still emptied without interrupting the heat supply.

The rest of the glassware is conventional laboratory equipment, and all

chemicals are reagent grade. The sodium hydroxide solution is made up by dissolving 1.5 pounds of sodium hydroxide in 2 liters of distilled water, adding 0.5 gram of Devarda's alloy, and boiling until volume is 1.8 liters. The mixed indicator of Ma and Zuazaga (2) is used.

PROCEDURE

Weigh about 100 mg. of sample into a 50-ml. beaker, and add 25 ml. of 1 to 1 hydrochloric acid and 1 ml. of hydrofluosilicic acid. Cover with a watch glass and heat just below boiling for 30 minutes. Add about 200 mg. of copper selenate. Digest until solution is complete.

Transfer the cooling sample solution to the Parnas-Wagner still and add 25 ml. of sodium hydroxide solution. Distill and collect the condensate in a 50-ml. Erlenmeyer flask containing 4 drops of mixed indicator solution, with 5 ml. each of 4% boric acid solution and distilled water. Adjust the heat input by a variable transformer so that 5 minutes after distillation begins, 10 ml. of condensate will have been collected. The boric acid solution (?) need not be accurately measured.

Titrate the collected ammonia with standard acid (about 0.07N), and make a blank determination using the same amount of reagents as in the sample determination.

RESULTS AND DISCUSSION

The preliminary work was performed on two samples of U_2N_3 and one of UN. The results given in Table I show that several digestion methods are suitable for analyzing UN. However, only the recommended procedure gives complete recovery of nitrogen in U_2N_3 .

To test the recommended procedures further two more samples of uranium

Table I. Per Cent Nitrogen in Uranium Nitrides

Sample	Method				Theoretical
	1	2	3	Recommended	
UN	2.6	5.5	5.5	5.5	5.6
U_2N_3					
Lot 1	Sample not decomposed	No sample	No sample	8.3	8.1
Lot 2	Sample not decomposed	6.9	7.3	8.6	8.1

Values are average of at least four determinations.

nitride were especially prepared by hydriding pure uranium metal, pumping off the hydrogen, and then reacting the finely divided uranium with a measured amount of nitrogen in a Sieverts apparatus (1). The samples were calculated to contain 8.6 and 7.8% nitrogen. On analysis by the recommended procedure, these two samples gave nitrogen percentages of 8.5 ± 0.1 and 7.7 ± 0.1 , respectively.

The use of selenium in the determination of nitrogen, mostly in organic materials (3), has been widely reported. The unique feature of this procedure is the action of the selenate ion rather than any other species of selenium. This action is not effective if copper

selenate is used in concentrated sulfuric acid medium, in Method 1. It is believed that in fuming sulfuric acid the selenate ion is removed, because selenic acid has a lower boiling point than sulfuric acid. Selenium in various forms has been considered catalytic in action, but in this case the effect may be partly due to the solvent action of the selenate ion on uranium nitrides.

To demonstrate that the selenate rather than the copper ion is essential to the digestion, potassium selenate and copper sulfate were tried on separate digestions. The copper sulfate had no effect, while the potassium selenate gave results identical to those obtained with copper selenate.

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Solid Scintillation Counting of Hydrogen-3 and Carbon-14 in Paper Chromatograms

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A MAJOR LIMITATION of gas-flow counting of low-energy β -rays in paper chromatograms is the relatively high degree of absorption that occurs inside the paper before the electrons can emerge to produce an ionizing event in the detector. A detector, scintillation grade anthracene in the form of microcrystals, has been incorporated inside the paper by an impregnation technique as differentiated from the liquid scintillation counting reported by Roucayrol, Oberhauser, and Schussler [*Nucleonics* **15**, 11, 104 (1957)]. Photons produced inside the matrix can be diffusely reflected out of the paper and into a

Table I. Results of Measurements of Inositol- H^3 and Glucose- C^{14} by Gas-Flow-Counting and Solid Scintillation-Counting Techniques

Sample	Windowless Strip Counter			Windowless Internal Counter			Solid Scintillation Counter		
	Net c.p.s.	Signal Noise	Efficiency, %	Net c.p.s.	Signal Noise	Efficiency, %	Net c.p.s.	Signal Noise	Efficiency, %
Inositol- H^3 (100,000 dps)	149	300	0.15	250	100	0.25	844	141	0.8
Glucose- C^{14} (200 dps)	23.4	47	12	33.2	13	17	1490	56	1.5
							32.1	12	16
							59.6	9	30
							126	5	63

suitable phototube. The gas-flow counting and solid scintillation-counting techniques are compared in Table I.

Known aliquots of radioactive solutions of inositol- H^3 or glucose- C^{14} were dried on 1-inch squares of Whatman

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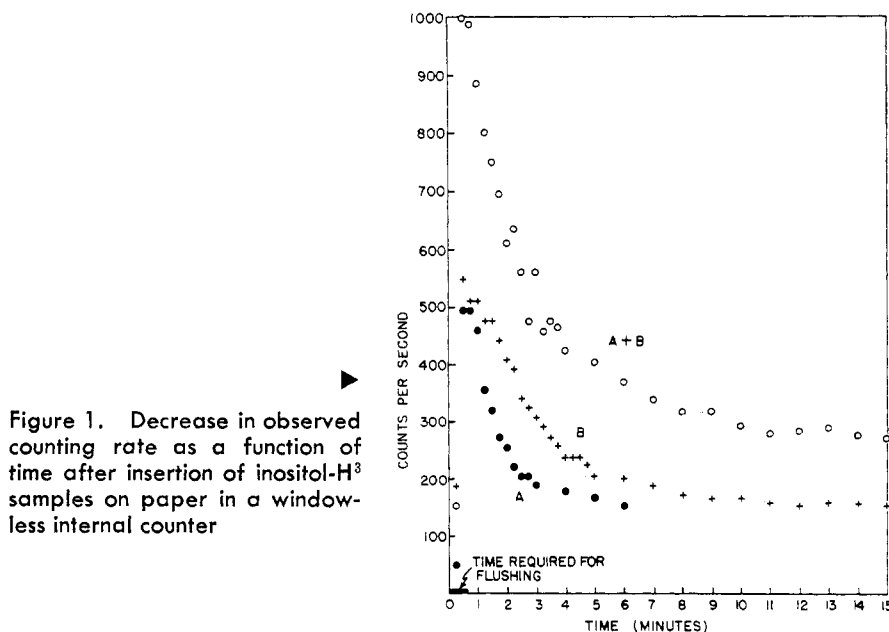


Figure 1. Decrease in observed counting rate as a function of time after insertion of inositol- H^3 samples on paper in a windowless internal counter

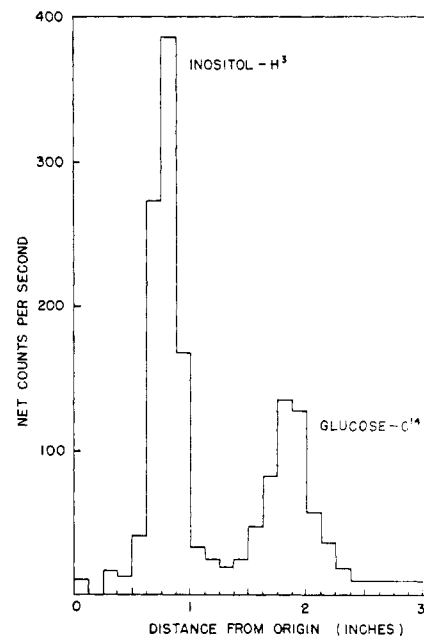


Figure 2. Solid scintillation counter scan of a paper chromatogram strip in which inositol- H^3 and glucose- C^{14} had been separated by chromatography in butanol-acetic acid-water 4:1:5, for 20.5 hours