results in a higher sensitivity than when stored in air. Such dependence on environment is not unexpected for an active electrode surface.

The results here suggest that the lead dioxide electrode is potentially applicable to the monitoring and investigation of a wide variety of titration reactions.

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Determination of Nitrogen in Vanadium Nitrides and Uranium Nitride (UN)

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FOR THE KJELDAHL determination of nitrogen in refractory nitrides, one of the most exasperating problems is the inability in some cases to dissolve appropriate amounts of sample without loss of nitrogen.

Silve Kallmann *et al.* (*1*) have shown that a hydrofluoric acid–phosphoric acid–potassium dichromate combination will dissolve various refractory metals rather rapidly. The method is also applicable to most carbides and nitrides. However, no mention was made of vanadium nitride, which is particularly troublesome with regard to the problem mentioned above.

Other workers (*2*, *3*) have gone to modifications of the Dumas method for the determination of nitrogen in uranium nitride and vanadium nitride. Morgenthaler and Menichelli (*4*) used a gasometric determination requiring the use of chlorine.

E. T. Turkdogan and E. M. Fenn (*5*) used the Dumas method for determining the amount of nitrogen in vanadium nitrides when they were investigating the variation of composition with temperature of vanadium nitrides under one atmosphere of nitrogen. At 900 °C, a nitride contained 20.5% nitrogen, but at 1500 °C it had decreased to 17.1% nitrogen. They reported that the vanadium nitrides have distinct composition ranges, the beta ranging from $VN_{0.57}$ to $VN_{0.49}$, and the gamma from $VN_{0.71}$ to $VN_{1.00}$. The fact that the vanadium nitrides are not stoichiometric may be a factor in the nitrogen losses occurring during the regular Kjeldahl determination.

Meyer, Parry, and Davis (*6*) successfully used tube furnace ignition and gas chromatographic determination of the nitrogen for determining nitrogen in various refractory nitrides, including vanadium nitride.

For uranium, UO_2, and uranium nitrides, Joan Lathouse, F. E. Huber, Jr., and D. L. Chase (*7*) and others (*8*, *9*) have shown that loss of nitrogen can occur in the dissolution process for Kjeldahl determinations. Cupric selenate and hydrofluosilicic acid used in the dissolving process and De Varda's alloy used during distillation helped in some cases to prevent losses. However, Sinclair, Davies, and Melhuish (*10*) reported results which show that cupric selenate promotes loss of nitrogen when uranium–plutonium dioxides were dissolved in a mixture of phosphoric and sulfuric acids.

Turovtseva and Kunin (*11*) suggest that insoluble residues be fused with potassium sulfate crystals and a mixture of phosphoric and sulfuric acid. Our experience with bisulfate fusion of vanadium nitride has been that temperatures high enough to decompose the nitrides invariably led to nearly complete loss of nitrogen.

To obtain accurate and simplified methods for nitrogen in vanadium nitrides and UN, various procedures were attempted. Kjeldahl procedures for vanadium nitrides and uranium nitride are given below.

EXPERIMENTAL

Apparatus used were two semimicro Kjeldahl distillation flasks, 270-ml capacity; an Erlenmeyer flask, 4-liter, thick-walled, with Nichrome wire heating assembly mounted through a rubber stopper as a steam generator; an acid digestion bomb with Teflon (Du Pont) cup; and other conventional laboratory glassware and equipment.

Reagents were sodium hydroxide solution–40% NaOH with H_2O, cool; sulfuric acid titrating solution–approximately 0.14*N*; boric acid solution, 1% with methyl red indicator. Combine 0.090 gram methyl red in 90 ml of ethyl alcohol, with 90 grams boric acid in 9 liters of H_2O. Make up and store in a $2^1/_2$ gallon solution bottle. The boric acid should be com-

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(10) V. M. Sinclair, W. Davies, and K. R. Melhuish, *Talanta*, **12,** 841–845 (1965).

(11) Z. M. Turovtseva and L. L. Kunin, "Analysis of Gases in Metals," Consultants Bureau, New York, 211–212 (1961).

Table I. Nitrogen in Vanadium Nitride, %

Sample	Nominal	Kjeldahl $HF-H_3PO_4-K_2Cr_2O_7$	Micro-combustion	Acid digestion bomb Kjeldahl 140 °C, HF
VN-10	8.84	6.6	9.6	8.26
powder	[a]	6.6	9.2	8.42
		6.8	9.7	8.16
			9.2	
VN-11	13.3	9.9	13.8	13.7
powder	[a]	10.2	14.0	13.8
		9.8	13.8	13.8
			13.7	
PC-285	21.2	10–17[c]	21.7	21.2
	[b]		21.2	21.4
			21.1	20.7
			21.4	

[a] Calculated from weight gain after exposure of high-purity vanadium to high-purity nitrogen at 1100–1200 °C.

[b] Reported value from laboratory supplying this material. Supplier also reported 78.6% V, 0.07% Fe, 0.07% O_2, and a few trace impurities; total = 99.94%.

[c] Kjeldahl, many runs made with various combinations of solvents (see discussion).

pletely dissolved and the solution made up to the full 9 liters before the indicator is poured in; otherwise a red precipitate will form.

Dissolution Procedures. VANADIUM NITRIDES. Weigh approximately 0.1-gram samples by difference into the Teflon cup of the acid digestion bomb. Add 10 ml of HF. Screw the cap of the bomb down tightly with the fingers and place the bomb in an oven maintained at 140–150 °C until the sample is dissolved. Up to four days has been required. The sample may be checked at any time by cooling the bomb to room temperature before opening and returning the bomb to the oven if the sample is not dissolved. When the sample has dissolved, transfer the solution quantitatively to the distillation apparatus.

URANIUM NITRIDE (UN). Weigh approximately 0.1-gram sample into a 50-ml beaker. Add 5 ml of phosphoric acid (H_3PO_4) and heat. After the H_2O has been driven off, heat covered until sample is in solution. Cool and dilute to 20 ml with H_2O. Stir carefully with a stirring rod to mix the water and acid. (The H_3PO_4 becomes thick and syrupy.) Transfer to the distillation apparatus when cool.

Description of Kjeldahl Distillation and Titration Method Used. Dissolved samples, made strongly alkaline with 40% NaOH solution were steam distilled in a semimicro Kjeldahl distillation apparatus. One hundred milliliters of distillate in each case were collected in a receiving beaker containing, originally, 10 ml of a 1% boric acid solution with methyl red indicator. Distillates were titrated with 0.14*N* sulfuric acid to the same end point (yellow to red). Deionized water was used to generate steam and used thoughout the determinations. The sulfuric acid was standardized with ammonium chloride carried through the distillation.

Blank Determinations. For high nitrogens (nitrides), blanks are not a significant factor (< 0.02% N with 0.1-gram sample). However, it is a good idea to carry a blank through the procedure to check for contamination.

Kjeldahl determinations should be made in an isolated area of the laboratory to prevent atmospheric contamination, and dissolved samples should not be allowed to stand around longer than necessary.

Safety Precautions. Care should be taken with the steam distillation apparatus to avoid any pressure buildups and exposure to hot steam.

RESULTS AND DISCUSSION

Table I gives the nitrogen content in vanadium nitride as determined by several methods. The Kjeldahl method, in any form other than with HF in the acid digestion bomb, failed with vanadium nitride. We suggest that molecular species (N_2) are formed in the dissolution process: samples were dissolved in airtight containers on a hot plate or in a water bath and cooled before opening, but results were still low. Also we tried many dissolution combinations involving HF, H_3PO_4, $HClO_4$, $K_2Cr_2O_7$, cupric selenate, and hydrofluosilicic acid. Either the sample would not dissolve or results were low and inconsistent.

When the ordinary Kjeldahl methods failed with vanadium nitrides, a simple microcombustion method was tried. Vanadium nitride samples were ignited in platinum boats in a microcombustion apparatus at 800 °C for 1 hour in flowing oxygen. Vanadium content was calculated from the weight of the V_2O_5 residues, and nitrogen obtained by difference. V_2O_5 residues were checked by the Kjeldahl procedure and were well under 100 ppm of nitrogen. It is recognized that the combustion technique may be valid only for rough approximations due to carbon, oxygen, or other impurities in the sample. For comparison purposes, the nitrogen values by this combustion method are shown in Table I, as are the nitrogen contents from the weight gain of high-purity vanadium as it was nitrided.

The Teflon-lined bomb values for the high-purity vanadium nitride (PC-285) indicate the Kjeldahl method is valid if vanadium nitride samples can be heated in a sealed container hot enough to dissolve with HF without an oxidizer.

Table II provides data of replicate runs of a uranium nitride sample over a period of 1 year. The Kjeldahl procedure was used after dissolving the sample in phosphoric acid only. The chromate method (5 ml H_3PO_4–15 ml HF–1 gram $K_2Cr_2O_7$ with about 0.1 gram of sample) is inadequate in this case. A loss of nitrogen results. We have found that H_3PO_4 alone is the most suitable solvent for uranium, UN, UC, and UN–UC–uranium oxide combinations.

Table II. Nitrogen in Uranium Nitride, UN Sample, %

Sample weight	Method	Number of determinations	Per cent, average	Per cent range	Stdard dev	Theoretical UN
0.1 g	Kjeldahl, H_3PO_4 solvent	28	5.78	5.71 to 5.84	0.035	5.56
0.1 g	Kjeldahl, Chromate method H_3PO_4-HF-$K_2Cr_2O_7$	8	3.48	3.28 to 3.74	0.164	5.56

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