

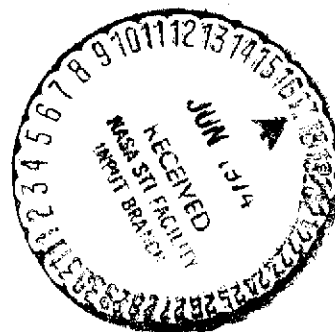
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## COMPARISON OF INERT-GAS-FUSION AND MODIFIED KJELDAHL TECHNIQUES FOR DETERMINATION OF NITROGEN IN NIOBIUM ALLOYS

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16. Abstract <p>This report compares results obtained for the determination of nitrogen in a selected group of niobium-base alloys by the inert-gas-fusion and the Kjeldahl procedures. In the inert-gas-fusion procedure the sample is heated to approximately 2700<sup>o</sup> C in a helium atmosphere in a single-use graphite crucible. A platinum flux is used to facilitate melting of the sample. The Kjeldahl method consisted of a rapid decomposition with a mixture of hydrofluoric acid, phosphoric acid, and potassium chromate; distillation in the presence of sodium hydroxide; and highly sensitive spectrophotometry with nitroprusside-catalyzed indophenol. In the 30- to 80-ppm range, the relative standard deviation was 5 to 7 percent for the inert-gas-fusion procedure and 2 to 8 percent for the Kjeldahl procedure. The agreement of the nitrogen results obtained by the two techniques is considered satisfactory.</p>			
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# COMPARISON OF INERT-GAS-FUSION AND MODIFIED KJELDAHL TECHNIQUES FOR DETERMINATION OF NITROGEN IN NIOBIUM ALLOYS

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## SUMMARY

This report compares results obtained for the determination of nitrogen below 100 ppm in a selected group of niobium-base alloys by modified Kjeldahl and inert-gas-fusion procedures. The designations and nominal compositions in weight percent of the alloys are as follows: B-66 (Nb-5Mo-5V-1Zr), Cb-752 (Nb-10W-3Zr), Nb-1Zr, C-129Y (Nb-10W-10Hf-0.1Y), WC-3015 (Nb-29Hf-15W-1Zr-4Ta), and FS-85 (Nb-28Ta-10W-1Zr).

The modified Kjeldahl method used consisted of a 2- to 3-hour dissolution of a 0.3- to 0.6-gram solid metal sample in a mixture of hydrofluoric acid, phosphoric acid, and potassium chromate; addition of excess sodium hydroxide; and distillation of the ammonia into dilute boric acid with argon used as a flushing gas. The sensitive nitroprusside-catalyzed indophenol reaction was used for the spectrophotometric measurement. The blank contained 4 to 8 micrograms of nitrogen. A significant portion of the blank was believed to be introduced from the laboratory atmosphere. The atmosphere was checked for ammonia while samples were being dissolved and analyzed.

The inert-gas-fusion procedure utilizes the Leco TC-30 simultaneous nitrogen-oxygen determinator. The sample is heated with 1 gram of platinum to approximately 2700° C in a helium atmosphere in a single-use graphite crucible. The released gases are separated chromatographically and measured in a thermal-conductivity cell. The sample analysis for both oxygen and nitrogen, including outgassing the crucible, takes 4 minutes. The high-temperature outgassing of the crucible by the impulse furnace results in low blanks, approximately 1 ppm for nitrogen and 3 ppm for oxygen.

Results are shown for the modified Kjeldahl and TC-30 techniques for the determination of nitrogen. Analyses were repeated on 2 days by each technique. For FS-85, the alloy which represents the most difficult case because it has the lowest nitrogen content, the relative standard deviation was 4.8 percent with the TC-30 procedure and 3.1 percent by the modified Kjeldahl procedure. Results for nitrogen by vacuum fusion were generally low for the alloys analyzed.

The agreement of the modified Kjeldahl and the TC-30 results for nitrogen is considered satisfactory. The fact that both nitrogen and oxygen results are obtained rapidly with good precision makes the TC-30 procedure very attractive for the analysis of niobium alloys.

## INTRODUCTION

Promising candidates for the skin material for the Space Shuttle are the following refractory alloys (nominal compositions in weight percent): B-66 (Nb-5Mo-5V-1Zr), Nb-1Zr, Cb-752 (Nb-10W-3Zr), C-129Y (Nb-10W-10Hf-0.1Y), FS-85 (Nb-28Ta-10W-1Zr), and WC-3015 (Nb-29Hf-15W-1Zr-4Ta). Nitrogen and other interstitial elements are critical to the strength and corrosion resistance of refractory metals at high temperature. Thus, it is important to monitor changes in nitrogen content and to determine nitrogen in these alloys below the 100 ppm level.

There has been only a limited amount of work reported on niobium metal showing a comparison of results obtained for nitrogen in the same material by two methods (ref. 1). This is due in part to the difficulty of dissolving refractory metals for the Kjeldahl nitrogen determination. Results that have been reported show no comparison of precision between instrumental and Kjeldahl nitrogen determinations.

Only after Kallmann, Hobart, Oberthin, and Brienza introduced an improved chemical dissolution procedure (ref. 2) was it possible to dissolve rapidly solid chunks of refractory metals such as tungsten, molybdenum, niobium, and tantalum for Kjeldahl nitrogen determinations. Two important advantages of this procedure were rapid sample dissolution and low-nitrogen blanks. These advantages facilitated the comparison of the Kjeldahl and instrumental methods. The same modified Kjeldahl procedure as used previously for two tantalum alloys (ref. 3) was used for the niobium alloys studied. The distillation procedure was adapted from one described by Ciaranello (ref. 4). The nitroprusside-catalyzed indophenol reaction was used for measurement of ammonia (refs. 5 to 11). The spectrophotometric procedure was that described by Mann (ref. 10).

Earlier work in our laboratory showed a comparison of a modified Kjeldahl and a vacuum-fusion gas analysis technique for the determination of nitrogen in two tantalum alloys (ref. 3). Because of the success with the tantalum alloys, a determination of the nitrogen content of the niobium alloys listed at the beginning of this section was attempted with a vacuum fusion gas analyzer. The niobium samples were added by the flux technique with direct contact of the sample and the platinum flux. The baths tried were platinum and platinum plus tin (80Pt-20Sn). The bath temperature was 2000<sup>o</sup> C. The nitrogen results obtained by vacuum fusion were one-half to two-thirds of the values obtained by the modified Kjeldahl procedure.

The tantalum alloys studied in the earlier comparison were subsequently analyzed on a Leco TC-30 nitrogen-oxygen determinator (TC-30). The nitrogen values obtained agreed with the results that had been obtained by vacuum fusion and the modified Kjeldahl procedures.

In the present investigation the niobium alloys were also analyzed on the TC-30. These nitrogen values agreed with those obtained by the modified Kjeldahl procedure. This could be attributed to the higher operating temperature of the TC-30, the single

bath, the single crucible, or a combination of all these factors. In addition to these factors, the presence of platinum is essential for complete release of nitrogen from the sample.

This report demonstrates the applicability of the TC-30 analyzer for the determination of nitrogen in six niobium alloys and compares the results with those of a modified Kjeldahl method.

Samples of the six niobium alloys used were taken from rods with a diameter ranging from 13 to 19 millimeters. The rods were sliced with a water-cooled abrasive wheel. The slices were then cut in half with a hand-operated, flat-bed shear. The halves were used for the two methods of analysis. The samples were analyzed on 2 days by each method. The same chemical etch was used for all samples.

### INSTRUMENTAL ANALYSIS

The classical vacuum-fusion and inert-gas-fusion techniques both involve high-temperature fusion of the sample in a graphite crucible, so that carbon reduction and thermal decomposition reactions may occur. Quantitative extraction of carbon monoxide for the determination of oxygen in the refractory metals can be achieved if optimal conditions are provided in the fusion crucible. Some molecular nitrogen is also evolved under the same conditions. As stated earlier, efforts in our laboratory to determine nitrogen in niobium alloys by vacuum fusion have always yielded lower values than the Kjeldahl procedure. Turovtseva and Kunin reported the determination of nitrogen by vacuum fusion in specially prepared samples of niobium (ref. 12). Dallmann and Fassel show a comparison of the Kjeldahl and inert-gas-fusion procedures for the determination of nitrogen in niobium metal by using a platinum-tin bath and a pyrolytic boron nitride thimble (ref. 1). We are not aware of any comparisons of instrumental and Kjeldahl nitrogen values for niobium alloys. Close agreement was not easily achieved for several reasons. First, at one time milled chips, not solid chunks, were used for Kjeldahl samples. However, this type of preparation may cause nitriding of the surface. The best sample form is the one with the least exposed surface. Second, former chemical dissolution procedures were neither rapid nor convenient. Third, as reported by Somiya, Hirano, Kamada, and Ogahara, if the same collection time as used for oxygen is used for the extraction of nitrogen, the nitrogen extraction is incomplete (ref. 13). Somiya and coworkers were able to overcome this problem in the analysis of steel samples by vacuum fusion by extending the collection time for nitrogen. Goward suggested that the problem is due to the difficulty of extracting nitrogen down to its equilibrium value (ref. 14).

Lemm demonstrated that quantitative recovery of nitrogen in steel was possible when a new small graphite crucible was used for each sample extraction under an inert

gas (ref. 15). Koch and Lemm demonstrated that nitrogen recovery progressively decreased when several steel samples were extracted in the same inert-gas-fusion crucible (ref. 16).

An instrument based on the principles of pulse heating described by Vasserman and Turovtseva and later used by Goldbeck is now commercially available as the TC-30 analyzer (ref. 17). In this instrument a high current is pulsed through a graphite crucible so that temperatures in excess of 2700<sup>o</sup> C are rapidly attained. A new graphite crucible is used for each determination. The nitrogen is separated from the oxygen by a chromatographic column. The nitrogen and oxygen are measured by thermal conductivity and their concentrations presented on separate digital voltmeters. An analysis for both nitrogen and oxygen can be done in less than 4 minutes. Although intended for the analysis of gases in steel, the TC-30 can be used for refractory metals by suitable adjustments in procedure and operating conditions. These adjustments include wrapping the sample in platinum to provide a fluid medium for dissolving the refractory metal and to achieve complete release of the nitrogen. The minimum amount of platinum required for the complete release of both nitrogen and oxygen was found to be three times the sample weight. The flux was a 1-gram platinum wire spiral which held the sample. The heating cycle was extended to 20 seconds to compensate for the larger mass of metal added to the crucible. Sample preparation is described in appendix A. Details of the instrumental analysis are given in appendix B.

### MODIFIED KJELDAHL PROCEDURE

At the present time, the method most often used for the determination of nitrogen is a modified Kjeldahl procedure. It is applicable to all metals and is usually regarded as more reliable and precise than vacuum fusion (ref. 18). At low concentrations (i. e. , 0 to 100 ppm), a spectrophotometric measurement is now used instead of the titrimetric finish used for higher amounts. Originally the Nessler procedure was used. Recently, the advantages of the indophenol spectrophotometric method have won it wide popularity.

There are several sources of ammonia nitrogen that cause high blanks in the Kjeldahl determination, such as chemical reagents and laboratory air. Purification of our reagents had only a slight effect on the blank. Prior to analysis, samples are commonly filed or chemically etched (or both). Very small or irregular samples are more easily etched than filed. In the work described in this report, all samples were etched with dilute hydrofluoric acid and hydrogen peroxide before both the modified Kjeldahl and the TC-30 analysis.

The chemical dissolution of metal samples by Kallmann's procedure greatly reduces exposure to atmospheric contamination. Samples are usually dissolved in less than 2 hours with a mixture of hydrofluoric acid, phosphoric acid, and potassium chromate.

Using loosely stoppered Teflon bottles allows samples to be dissolved without addition of more acid and further minimizes exposure to laboratory air.

The size and variation of the blank in the Kjeldahl method has previously made unreliable the determination of less than 25 ppm nitrogen. In our laboratory, the blank usually amounts to 4 to 8 micrograms of nitrogen, of which a major part is attributed to atmospheric contamination. The laboratory air is monitored for ammonia by a procedure similar to that of Leithe and Petschl (ref. 19).

The present report describes several modifications of the Kjeldahl apparatus and procedure for the determination of nitrogen in the niobium-base alloys. The modified method has advantages over similar ones commonly used. The first modification to the apparatus (see fig. 1) is to use a larger distillation flask (300 cm<sup>3</sup>) in order to accommodate the large amount of salts formed by the addition of excess sodium hydroxide to hydrofluoric acid, phosphoric acid, and potassium chromate solutions of refractory metals. The round-bottom distillation flask has an outer 29/42 standard taper joint and is sealed with an ethylene-propylene O-ring on the inner joint. This prevents the joint from "freezing" and permits easy disassembly for cleaning after contact with caustic solutions. The diameter of the lower 12 centimeters of the gas inlet tube was increased from 8 to 11 millimeters in order to prevent salts from clogging the tube during the distillation. The rest of the distillation apparatus is standard, as may be seen from the figure.

The next modification from common Kjeldahl practice is the use of an inert carrier gas and direct heating of the distillation flask instead of the usual flow of steam. This change makes the manipulations easier and faster.

The intense blue indophenol color given by the reaction of ammonia with phenol and hypochlorite was first observed by Berthelot in 1859 (ref. 20). The sensitivity of the indophenol procedure can be further increased by the presence of various catalysts. Chaney and Marbach (ref. 5) were the first to recommend the use of sodium nitroprusside as a catalyst. This reagent not only accelerates the speed of the reaction but also increases to a maximum the conversion of ammonia to indophenol. The procedure described in this report is similar to one recommended by Mann (ref. 10). In this procedure 1 microgram of ammonia nitrogen in a 100-cubic-centimeter volume gives an optical density of 0.016 absorbance units when measured in a 1-centimeter cell at 630 nanometers. This is equivalent to a molar absorptivity of  $22.4 \times 10^6$  cubic centimeters per mole per centimeter and is exactly the same sensitivity reported by Bach, Willis, and Reid (ref. 6), who used a slightly different indophenol procedure.

The principal advantage of high sensitivity is that relatively small samples of solid material are sufficient for determination of low nitrogen content. Such small samples may now be dissolved rapidly with a minimum of atmospheric contamination that determination of less than 25 ppm nitrogen is possible with a higher degree of precision than was formerly possible.

The apparatus, reagents, and procedure used are the same as those described in an earlier publication for the comparison of a modified Kjeldahl and a vacuum-fusion technique for the determination of nitrogen in tantalum alloys. All procedural steps remained the same except for the use of a 0.5-gram sample, due to the higher nitrogen content of the niobium alloys. The etchant used is described in appendix A.

## DISCUSSION OF RESULTS

The data reported in table I indicate that equivalent results for the determination of nitrogen in the selected niobium alloys are obtained by the TC-30 and the modified Kjeldahl methods. The precision of the TC-30 results is not significantly different from the precision of the modified Kjeldahl results. In the range 30 to 80 ppm nitrogen, the relative standard deviation was 2 to 8 percent by the modified Kjeldahl method and 5 to 7 percent by the TC-30 method.

The mean values for nitrogen by the two methods agree within 5 ppm for five of the alloys tested. For the alloy Cb-1Zr, the difference in the nitrogen mean values is 10 ppm, the higher value of 80 ppm being obtained by the TC-30 method.

The samples were analyzed on 2 days by both methods. The blank values reported are a range of blanks for the 2 days for each method. The blank for the TC-30 method is lower and less variable than the blank for the modified Kjeldahl method. This should be expected because in the instrumental analysis the sample is not exposed to as many operations, such as dissolution, distillation, and colorimetric measurement. Moreover, exposure to the laboratory atmosphere may cause significant contamination by absorption of airborne ammonia in the Kjeldahl method but not in the instrumental.

## SUMMARY OF RESULTS

The inert-gas-fusion and modified Kjeldahl techniques for determination of nitrogen in niobium alloys were compared. The analytical and precision data demonstrated the applicability of the inert-gas-fusion technique for the determination of nitrogen in six niobium alloys. The nitrogen values were obtained simultaneously with the determination of oxygen and had an accuracy and precision equivalent to modified Kjeldahl values. The TC-30 operating conditions could be accurately reproduced, the blank was low and constant, and the nitrogen and oxygen values were obtained from the same sample specimen. The analysis time per sample for the instrumental method was less than 4 min-



utes as compared to several hours or more for the modified Kjeldahl procedure. Elimination of acid dissolution and the laboratory atmosphere as sources of contamination resulted in a lower and less variable blank.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, March 15, 1974,  
501-01.

## APPENDIX A

### SAMPLE PREPARATION

The sample rods were sliced with a water-cooled abrasive wheel. The slices were cut in half with a flat-bed shear. One half of the slice was used for the TC-30 determination, and the remaining half slice was used for the modified Kjeldahl determination. Normally, samples for gas analysis are cleaned by filing. This method is tedious with small or irregularly shaped samples. Acid etching was chosen because it allows easier reproduction of a uniformly clean surface. The etch solution consisted of 10 cubic centimeters of 1:1 hydrofluoric acid and a few drops of 30 percent hydrogen peroxide in a Teflon beaker. The solution was warmed for a few minutes to accelerate the etching. Etching was stopped when a matte finish appeared on the samples. Following etching, the samples were rinsed with distilled water, acetone, and finally reagent grade ethyl ether. After drying at 110<sup>0</sup> C, the samples were weighed. The sample intended for the modified Kjeldahl determination was placed in a Teflon bottle. The sample for instrumental analysis was placed in a platinum wire spiral. This spiral was formed from a piece of 20-gage low-oxygen platinum. The weight of platinum used for each sample was 1 gram. The ends of the spiral were closed so as to contain the sample.

## APPENDIX B

### INSTRUMENTAL ANALYSIS PROCEDURE

The instrument used to obtain the nitrogen values reported was a Leco Corporation Model TC-30 simultaneous nitrogen-oxygen determinator. The sample is fused in a helium atmosphere at a high temperature in a small, single-use graphite crucible. The graphite crucible is held between water-cooled electrodes and attains a temperature of 2700<sup>0</sup> C when a high amperage current is applied for 20 seconds. Prior to the sample analysis, the graphite crucible is outgassed at the operating temperature for 45 seconds. The sample, 0.2 to 0.3 gram of niobium alloy contained in a 1-gram platinum spiral is dropped into the crucible. The minimum amount of platinum must be three times the weight of the sample. Again the crucible and sample are heated. Helium carries the released gases over copper oxide, where the carbon monoxide is oxidized to carbon dioxide and the hydrogen is oxidized to water. The water is absorbed in magnesium perchlorate, and the remaining nitrogen and carbon dioxide are separated chromatographically on a silica gel column. Less than 1 minute after the end of the burn, the nitrogen leaves the chromatographic column and enters the measuring conductivity cell and is recorded. The bridge output is displayed on an electronic digital voltmeter. The oxygen peak is recorded in the measuring cell about 1 minute later and is similarly measured and displayed. One sample can be analyzed for nitrogen and oxygen in less than 4 minutes. Outgassing and analysis cycles are initiated by pushbutton operation. Both cycles are automatically controlled by electronic timers and solenoid valves.

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TABLE I. - COMPARISON OF RESULTS FOR DETERMINATION OF NITROGEN IN SIX NIOBIUM ALLOYS BY MODIFIED KJELDAHL AND TC-30 INERT-GAS-FUSION METHODS

Alloy	TC-30 inert-gas-fusion method					Modified Kjeldahl method				
	Number of values	Mean, ppm	Standard deviation, S, ppm (a)	Relative standard deviation, percent (b)	Blank range, $\mu\text{g}$ (c)	Number of values	Mean, ppm	Standard deviation, S, ppm (a)	Relative standard deviation, percent (b)	Blank range, $\mu\text{g}$ (d)
FS-85	12	33	1.6	4.8	0.0-0.5	8	38	1.2	3.1	4.1-5.8
Cb-752	13	39	2.4	6.1	0.5-1.5	10	41	3.2	7.8	5.3-8.8
C-129Y	10	45	2.3	5.1	0.5-1.0	11	46	3.1	6.7	5.3-8.8
WC-3015	14	60	3.1	5.2	0.5-1.0	10	55	1.4	2.5	5.0-7.1
Nb-1Zr	10	80	3.8	4.7	0.5-1.5	12	70	1.3	1.8	5.0-7.1
B-66	10	75	5.2	6.9	0.0-0.5	10	79	2.1	2.6	4.1-5.8

<sup>a</sup>

$$S = \sqrt{\sum d^2 / (n - 1)}, \text{ where } d \text{ is the deviation from the mean and } n \text{ is the number of determinations.}$$

<sup>b</sup>Relative standard deviation is (S)(100)/mean.

<sup>c</sup>Blank reported is range of three to four determinations for each of 2 days.

<sup>d</sup>Blank reported is range of four to six determinations for each of 2 days.

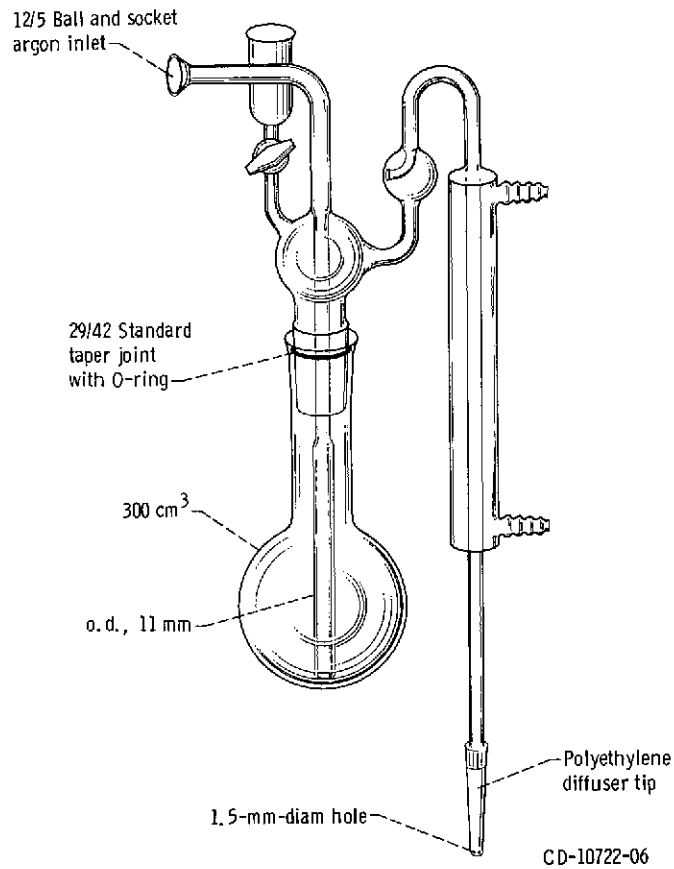


Figure 1. - Modified Kjeldahl distillation apparatus.