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INTERLABORATORY COMPARISON OF CHEMICAL ANALYSIS OF URANIUM MONONITRIDE

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16. Abstract Analytical methods were established in which the critical variables were controlled, with the result that acceptable interlaboratory agreement was demonstrated for the chemical analysis of uranium mononitride. This was accomplished by using equipment readily available to laboratories performing metallurgical analyses. Agreement among three laboratories was shown to be very good for uranium and nitrogen. Interlaboratory precision of ± 0.04 percent was achieved for both of these elements. Oxygen was determined to ± 15 parts per million (ppm) at the 170-ppm level. The carbon determination gave an interlaboratory precision of ± 46 ppm at the 320-ppm level.			
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SUMMARY

Uranium mononitride (UN) is a promising nuclear fuel for future lithium-cooled space power reactors. In the past, metallography, microstructural analysis, and chemical analysis have been used to characterize UN. The usefulness of chemical analysis for this purpose has been limited by problems associated with the determination of uranium and nitrogen. In 1969, four laboratories cooperated in a comparative chemical analysis of UN. Results of this work showed that uranium could be determined with an interlaboratory precision of ± 0.15 percent. The nitrogen determination yielded an interlaboratory precision of ± 0.08 percent.

The present work was undertaken to improve the precision of both the uranium and nitrogen determinations. For this purpose, the analytical procedures for determining uranium and nitrogen were modified. Analytical procedures for the impurity elements oxygen and carbon, which had been determined in the earlier work, were also modified. An oxidation-reduction-oxidation method was used for uranium. The Kjeldahl method, following phosphoric acid dissolution, was used for nitrogen. Inert-gas fusion in a platinum bath was used for oxygen. The combustion-chromatographic method was used for carbon.

Both the uranium and nitrogen methods of determination were improved and resulted in an interlaboratory precision of ± 0.04 percent. Oxygen was determined to ± 15 parts per million (ppm) at the 170-ppm level. The interlaboratory precision for the determination of carbon, which was ± 46 ppm at the 320-ppm level, was an improvement over the earlier work. Results of the carbon determinations show very good intralaboratory precision combined with a large range for the mean carbon value. Further work should concentrate on identifying and eliminating the source of this discrepancy.

INTRODUCTION

Uranium mononitride (UN) is a promising nuclear fuel for space power reactors. In the past, metallography was relied upon for the characterization of UN. Microstructural analysis provided only qualitative information such as the presence or absence of uranium oxides or free uranium. Chemical analysis has also been used to characterize UN (refs. 1 and 2). In 1969, a comparative chemical analysis experiment, or round robin, was conducted by Oak Ridge National Laboratory under a contract for NASA (ref. 2). One of the objectives of this round robin was to "evaluate the nature of any existent problems" in the chemical analysis of sintered UN. The elements uranium, nitrogen, oxygen, and carbon were determined by four laboratories on two different sintering runs of UN. As a result of this round robin, it was reported that problems associated with the analysis for uranium and nitrogen prevented acceptable precision and accuracy in the analysis of UN. For uranium determinations, a precision of at least 1 part in 1000 was needed, and 1 part in 5000 was preferred. For nitrogen determinations, a precision of 1 part in 500 was needed.

The present round robin was initiated to modify procedures of analyses and to define operating parameters in order to improve the precision of the uranium and nitrogen determinations. The methods for oxygen and carbon were also modified. For oxygen the determination of the analytical precision was made for concentrations significantly lower than that in the earlier round robin. Three analytical laboratories cooperated in this study, namely, a producer, a user, and a commercial laboratory. All were experienced in the chemical analysis of sintered UN. The specific objectives were

- (1) To establish methods, using readily available equipment, which through careful control of variables would produce results which would have acceptable inter-laboratory agreement
- (2) To find what precision could be expected, using these methods, in the determination of the constituent elements of UN and the interstitial impurities carbon and oxygen
- (3) To provide a means for the exchange of information between participating laboratories about special handling, sample preparation, apparatus, and procedures

The precision referred to under objective (2) is the degree of mutual agreement between individual measurements, namely repeatability and reproducibility. Repeatability is the standard deviation of results obtained by the same operator using the same instrument in successive measurements. Reproducibility is the standard deviation of results obtained by different operators using the same or different types of instruments in different laboratories.

The UN used in this investigation was prepared by the hydride-dehydride-nitride process (ref. 2). The powdered UN was consolidated by isostatic pressing and sintering (ref. 3). Three rods about 23 centimeters long, 1 centimeter in diameter, and each approximately 100 grams in weight, were sintered at one time. Subsequently, the rods were broken into three pieces of equal size under a protective argon atmosphere. To avoid contamination during shipping, these samples were sealed under argon in a brass capsule (fig. 1). These samples were used for the interlaboratory analyses.

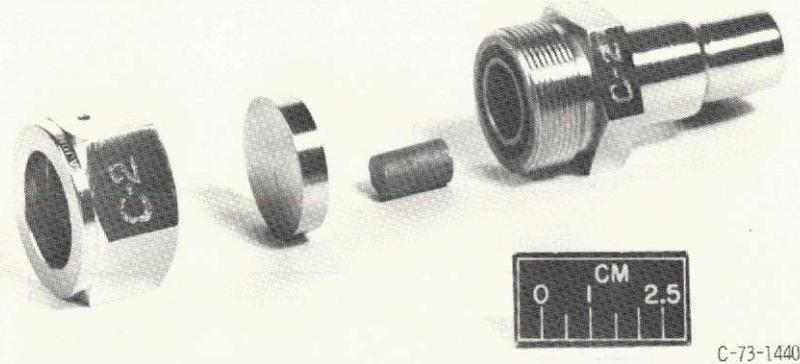


Figure 1. - Capsule used to ship sample.

EXPERIMENTAL PROCEDURES

A brief discussion of the procedures investigated for each element is given here. The method of sample preparation is described in appendix A. The chemical analysis methods that were finally used are fully described in the appendixes and briefly summarized in tables I to IV.

TABLE I. - CONDITIONS FOR DETERMINATION OF
OXYGEN BY INERT-GAS FUSION METHOD

Sample weight, g	0.25 to 0.5
Sample container	Platinum (foil or tube)
Bath metal	Platinum
Bath-to-sample ratio	10:1 (minimum)
Crucible temperature, °C	2100
Extraction time, min	3 to 4
Furnace carrier gas	Helium or argon
Furnace carrier gas flow, cm ³ /min	1000
Furnace carrier gas pressure, N/cm ²	6.9 (10 psi)
Analyzer carrier gas	Helium
Analyzer carrier gas flow, cm ³ /min	60
Analyzer carrier gas pressure, N/cm ²	13.8 (20 psi)

TABLE II. - CONDITIONS FOR DETERMINATION OF
CARBON BY COMBUSTION-CHROMATOGRAPHIC METHOD

Sample weight, g	0.3 to 0.5
Accelerator weight, g	1.0 iron plus 0.5 copper oxide
Oxygen pressure, N/cm ²	6.9 (10 psi)
Oxygen flow, cm ³ /min	1000
Helium pressure, N/cm ²	13.8 (20 psi)
Helium flow, cm ³ /min	60
Combustion time, min	2 to 3

TABLE III. - CONDITIONS FOR DETERMINATION OF
URANIUM BY OXIDATION-REDUCTION-OXIDATION METHOD

[Sample weight, 3 to 4 g.]

Condition	First oxidation	Reduction	Second oxidation
Temperature, °C	1000	1000	1000
Gas	Instrument air	95 Percent argon, 5 percent hydrogen	Instrument air
Flow, cm ³ /min	300	300	300
Time, hr	2 to 3	1.5	2

TABLE IV. - CONDITIONS FOR DETERMINATION OF
NITROGEN BY THE KJELDAHL

DISTILLATION-TITRATION METHOD

Sample weight, g	0.5
Dissolution of sample	10 cm ³ of 85 percent ortho-phosphoric acid at 200° C
Separation of ammonia . . .	Steam distillation with 40 cm ³ of 50 percent sodium hydroxide
Absorption of ammonia . . .	20 cm ³ of 2.5 percent boric acid
Titrant for ammonia	0.2 N sulfuric acid
Indicator	2 drops of methyl purple solution

Uranium

Two gravimetric procedures were compared for the determination of uranium. One method is referred to as the direct oxidation method. This involves igniting the sample under a specific oxygen pressure and determining the uranium by weighing the resulting uranium octa-oxide (U_3O_8) (ref. 1). The other method, the one that is recommended, is the oxidation-reduction-oxidation method. The oxide resulting from ignition of UN in air is reduced with an argon-hydrogen mixture and then finally reoxidized in air to U_3O_8 . Both methods depend on the oxidation to U_3O_8 of a sample that is free of appreciable amounts of metallic and nonmetallic impurities.

We believe that, during oxidation of UN particles in air, a protective oxide coating may form which inhibits complete oxidation. Reduction then breaks the particles down into smaller UO_2 particles which are then susceptible to complete oxidation to U_3O_8 . In addition, the oxygen content of the sweep gas was found to be critical in the direct oxidation method. The oxidation-reduction-oxidation method was adopted for these reasons and because larger samples could be used. The adopted method is described in appendix B.

Nitrogen

The Kjeldahl method (refs. 4 and 5), as modified, uses phosphoric acid dissolution and is limited to samples of uranium mononitride because the sesquinitride is insoluble in this acid. However, the Dumas method is applicable to the determination of nitrogen in both nitrides.

The Kjeldahl and the Dumas methods were compared for the analysis of nitrogen in UN. The mean nitrogen value by the Kjeldahl method was 5.47 ± 0.02 percent, compared with a mean of 5.46 ± 0.01 percent for the Dumas method. The Kjeldahl method was selected for its simplicity and readily available apparatus and because a larger sample weight could be used. The Kjeldahl method used is described in appendix C.

Oxygen

Oxygen was determined by the inert-gas fusion procedure. Vacuum fusion analysis was not considered because the equipment is not as readily available and the procedure is more time consuming. Samples of UN encapsulated in platinum were added to a graphite crucible containing a platinum bath at $2100^{\circ}C$. The oxygen released combines with carbon to form CO and is subsequently oxidized to CO_2 and measured chromato-

graphically. The inert-gas fusion method for the determination of oxygen is described in appendix D.

Carbon

Carbon was determined by combustion chromatography. The accelerators tested were granular tin and copper, preignited iron, and iron with wire-form copper oxide. The accelerator finally agreed upon was iron plus copper oxide. The combustion-chromatographic method used for the determination of carbon is described in appendix E.

RESULTS AND DISCUSSION

Chemical analyses for uranium, nitrogen, oxygen, and carbon were performed on samples of sintered UN at three different laboratories. Two rounds of analyses were conducted for uranium and nitrogen, while three were run for oxygen and carbon. The participants met after the first and second round to examine and discuss their results. At this time, ground rules for further work were discussed and agreed upon.

Tables V to VIII summarize the results of the analysis of UN. The tables list the results of the final round only. All the values shown were obtained by using the appropriate methods described in the appendixes.

Uranium

Results for uranium are shown in table V. The mean of all results is 94.44 percent with a standard deviation of 0.04 percent and a relative standard deviation of 0.04 percent.

Nitrogen

Nitrogen results are shown in table VI. The mean of all results is 5.46 percent. The standard deviation is 0.04 percent, and the relative standard deviation is 0.73 percent.

TABLE V. - DETERMINATION OF URANIUM

Laboratory	Uranium content, percent					Mean uranium content, percent	Standard deviation ^a , S, percent	Relative standard deviation ^b , percent
1	94.44	94.47	94.48	94.47	94.46	94.46	0.02	0.02
2	94.43	94.47	94.45	94.48	94.46	94.46	.02	.02
3	94.38	94.40	94.38	94.40	94.39	94.39	.01	.01
Pooled results						94.44	0.04	0.04

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

^b The relative standard deviation is $\frac{S \times 100}{\text{Mean}}$.

TABLE VI. - DETERMINATION OF NITROGEN

Laboratory	Nitrogen content, percent					Mean nitrogen content, percent	Standard deviation ^a , S, percent	Relative standard deviation ^b , percent
1	5.43	5.47	5.44	5.46	5.45	5.45	0.02	0.37
2	5.48	5.43	5.47	5.48	5.46	5.46	.02	.37
3	5.41	5.42	5.60	5.45	5.52	5.48	.08	1.4
Pooled results						5.46	0.04	0.73

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

^b The relative standard deviation is $\frac{S \times 100}{\text{Mean}}$.

Oxygen

All the laboratories experienced more problems with oxygen and carbon determinations than with either of the major elements. The sensitivity of UN to contamination by oxygen made it necessary to use special techniques in the shipping, storage, and sample preparation steps. An inert cover gas was used by each laboratory to protect the samples at all stages of preparation and storage.

The first round for oxygen served as a test to find which measures were essential to keep oxygen contamination to a minimum. After the second round, the procedure was modified to specify a minimum bath temperature of 2100°C to ensure complete recovery of oxygen from the sample. For the third round a sample of zirconium metal was distributed to each laboratory for oxygen analysis. The zirconium metal was to be analyzed just before the determination of oxygen in the UN sample. The nominal oxygen value for this zirconium sample was 160 ± 10 ppm. The zirconium sample was intended to serve as an independent check to verify that each laboratory was using a crucible temperature high enough to recover all the oxygen from the UN samples. The third round was then run using the oxygen method detailed in appendix D. Table VII presents data for oxygen in UN from the third round.

Set A for laboratory 3 represents the UN sample originally distributed for the third round for oxygen analysis. These results were compared with those of laboratories 1 and 2 and earlier rounds in which laboratory 3 reported mean oxygen values of 173 and 179 ppm. Then a piece of UN left over from laboratory 2 was sent to laboratory 3 for analysis. This sample was analyzed and reported as set B.

Laboratories 1 and 2 reported 156- and 162-ppm oxygen, respectively, in the zirconium sample. Laboratory 3 reported a value of only 113 ppm even though pyrometer readings indicated a crucible temperature of 2100°C . This oxygen value was 71 percent of the average values of laboratories 1 and 2. The oxygen in UN for laboratory 3 (set A) was 70 percent of the average values of laboratories 1 and 2. The exact reasons for the lower values in set A are not known. However, based on the low recovery of oxygen from the zirconium sample, all set A values were rejected. If set A oxygen values are replaced by those of set B, an overall mean of 171 ppm with a standard deviation of 15 ppm and a relative standard deviation of 8.8 percent is obtained.

Carbon

Just as for oxygen, three rounds were run for carbon. In the first round a variety of accelerators were tried before the carbon method in appendix E was agreed upon. Results of the third round for carbon are listed in table VIII.

TABLE VII. - DETERMINATION OF OXYGEN

Laboratory	Oxygen content, ppm					Mean oxygen content, ppm	Standard deviation ^a , S, ppm	Relative standard deviation ^b , percent
1	174	168	165	183	170	172	7.0	4.1
2	187	180	179	190	175	182	6.1	3.4
3 (set A)	136	141	110	121	110	124	14.4	11.6
3 (set B)	164	138	173	185	139	160	20.8	13.0
Pooled results (excluding set A)						171	15.0	8.8

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

^bThe relative standard deviation is $\frac{S \times 100}{\text{Mean}}$.

TABLE VIII. - DETERMINATION OF CARBON

Laboratory	Carbon content, ppm					Mean carbon content, ppm	Standard deviation ^a , S, ppm	Relative standard deviation ^b , percent
1	264	268	262	279	279	270	8.1	3.0
2	367	383	368	377	379	375	7.0	1.9
3	308	316	317	314	^c 257	314	4.0	1.3
Pooled results						320	46.0	14.0

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

^bThe relative standard deviation is $\frac{S \times 100}{\text{Mean}}$.

^cValue rejected because it exceeds three times the standard deviation.

A datum point for laboratory 3 was rejected since it was much more than three times the standard deviation from the mean. Combining all the results in the table gives a mean of 320 ppm and a standard deviation of 46 ppm. The relative standard deviation is 14 percent.

The participating laboratories were able to achieve satisfactory agreement for uranium and nitrogen using the recommended procedures of analysis. The degree of agreement for uranium was particularly good. Individual laboratories had repeatabilities of 0.01 to 0.02 percent. The reproducibility, the standard deviation of the combined laboratories, was 0.04 percent, which gives a precision of at least 1 part in 2300. This is well within the needed precision referred to in the INTRODUCTION.

The goal of determining nitrogen to a precision of 1 part in 500 was not reached although two of the three laboratories had very good repeatabilities. However, the reproducibility of 0.04 percent is an improvement of as much as a factor of 2 over that of the earlier UN round robin in 1969.

In the earlier round robin, oxygen ranged from 2000 to 4000 ppm and carbon from 200 to 600 ppm (ref. 2). The UN prepared for the present study contained considerably less oxygen. The carbon level was close to the low end of the range in the UN used in the 1969 round robin. Reasonable goals for interlaboratory agreement at these levels were set by the Materials Advisory Board for the comparison of chemical analyses of refractory alloys (ref. 6). When these goals are used, the target for the interlaboratory standard deviation at the 170-ppm level is 15 ppm. At the 320-ppm level the target standard deviation is 24 ppm. The cooperators in the present round robin did reach this goal for oxygen. However, the larger intralaboratory scatter of laboratory 3 indicates that the procedure for sampling and/or analysis could be further refined.

In the case of carbon the reproducibility is about twice the target of 24 ppm. Each laboratory achieved very good intralaboratory agreement, but the interlaboratory agreement was poor. However, the reproducibility figure is still useful until future work identifies and corrects the cause of this difference.

SUMMARY OF RESULTS

Three laboratories with experience in metallurgical analyses cooperated in the modification and testing of methods for the chemical analysis of uranium mononitride. The elements determined were uranium, nitrogen, oxygen, and carbon.

The reproducibilities of the uranium and nitrogen determinations were both ± 0.04 percent - an improvement over the previous values of ± 0.15 and ± 0.08 percent, respectively. For oxygen the reproducibility was ± 15 ppm at the 170-ppm level. Although the laboratories had very good repeatabilities for the carbon determination,

the largest being 8 ppm, the reproducibility was ± 46 ppm at the 320-ppm level. The spread in carbon results appears to be caused by unresolved differences among the laboratories.

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Cleveland, Ohio, October 25, 1973,
502-21.

APPENDIX A

SAMPLE PREPARATION

The solid UN sample was removed from its protective container in a glove box under an atmosphere of purified argon. The sample was broken into approximately 1- to 2-millimeter pieces with a Plattner mortar and pestle. A magnet was passed over the crushed sample to remove iron particles which may have been introduced from the mortar and pestle.

Sample weighing for carbon, nitrogen, and uranium was done outside the glove box. Samples for oxygen analysis were prepared under the protective cover of argon. This preparation included weighing the sample, encapsulating it in platinum, and placing the sample in a transfer vial with a screw cap. This vial was then placed into another larger screw-cap vial and closed. The prepared oxygen samples were stored in the glove box and analyzed within 24 hours.

Each laboratory used different protective enclosures for sampling. One used a glove box with recirculating argon, another used a glove box with flowing argon, and another used a folding plastic glove bag filled with argon.

APPENDIX B

OXIDATION-REDUCTION-OXIDATION COMBUSTION METHOD FOR URANIUM

Apparatus

A platinum boat 9.5 centimeters by 1.3 centimeters by 1 centimeter, or dimensions which will allow its insertion into the hot zone of a combustion tube, holds the sample. The boat is covered with a 45-mesh platinum gauze. A Vycor combustion tube 2.5 centimeters in inside diameter is placed into a tube furnace that will maintain at least 1000° C. A flowmeter with a range of at least 300 cubic centimeters per minute is attached to the furnace tube.

Gases

The gases used were instrument air, pure argon, and a mixture of 95 percent argon and 5 percent hydrogen.

Procedure

The combustion tube is purged with an argon flow of 300 cubic centimeters per minute while the furnace temperature is increased to 400° C. About 3 grams of UN is weighed into a tared platinum boat which is then covered with a tared platinum gauze. The total weight of sample, boat, and gauze is obtained. The covered boat is placed in the combustion tube. The temperature is increased to 1000° C, and the sweep gas is switched from argon to instrument air at a flow rate not exceeding 300 cubic centimeters per minute. After the temperature reaches 1000° C, heating is continued for 2 to 3 hours. Then the tube is cooled to 400° C, and the sweep gas is switched back to argon.

Then the gas is switched to the hydrogen-argon gas mixture, and the temperature is increased to 1000° C. Heating is continued at this temperature for 1½ hours. The sweep gas is switched back to argon and the combustion tube is purged. Then the sweep gas is switched back to instrument air at a flow rate not exceeding 300 cubic centimeters per minute at 1000° C for 2 hours. The combustion tube is cooled to 400° C using the argon sweep gas. Then the boat is removed and cooled in a desiccator for ½ hour. The boat is weighed and the weight of U₃O₈ is determined. The percentage of uranium is calculated as follows:

$$\text{Percent U} = \frac{\text{Grams U}_3\text{O}_8 \times 84.7997}{\text{Grams UN}}$$

An alternate procedure is to place the sample in a platinum crucible, cover it with gauze, and oxidize in a muffle furnace at 900°C . For reducing the sample, the platinum crucible is placed in a Rose crucible. The air is expelled with argon. The sample is heated with a blast lamp and reduced with pure hydrogen. Then it is oxidized and weighed as above.

APPENDIX C

KJELDAHL DISTILLATION-TITRATION METHOD FOR NITROGEN

Apparatus

A Kjeldahl distillation apparatus similar to ASTM apparatus number 14C (ref. 5) was used, except that the sample distillation flask was 300 cubic centimeters in volume.

Reagents

The reagents used were

- (1) Orthophosphoric acid, 85 percent
- (2) Boric acid solution, 2.5 percent
- (3) Sodium hydroxide solution, 50 percent
- (4) Sulfuric acid, 0.2 N, Fisher SO-A-218
- (5) Methyl purple indicator solution, Fisher SO-1-9
- (6) Standard ammonium chloride solution, 1 cubic centimeter = 3.0 milligrams of nitrogen. Ammonium chloride (1.1458 g dried at 110^o C) is transferred to a 100-cubic-centimeter flask and dissolved in water. The flask is filled to the mark with water, and the solution is mixed well.

Procedure

Approximately 0.5 gram of small chunks of UN is weighed into a 100-cubic-centimeter beaker. Seven to 10 cubic centimeters of 85 percent orthophosphoric acid are added. The beaker is placed on a hot plate at a temperature of at least 200^o C and heated until the sample is dissolved. Auxiliary heating with an infrared lamp will hasten the dissolution. Deionized water is added to dissolve the glassy mass. The solution is transferred to the distillation flask of the Kjeldahl apparatus after the beaker is checked for complete sample dissolution. More deionized water is added as necessary to cover the steam inlet tube.

Twenty cubic centimeters of 2.5 percent boric acid solution is placed in a 125-cubic-centimeter Erlenmeyer receiving flask and 2 drops of methyl purple indicator solution are added. The receiving flask is placed under the distillation apparatus condenser tip. Forty cubic centimeters of 50 percent sodium hydroxide solution is slowly added into the distillation flask to prevent suckback of the boric acid into the distillation flask. Steam distillation is continued for 20 minutes. The receiving flask is removed and the condenser tip is rinsed with deionized water. The absorbed ammonia is titrated in the

distillate with 0.2 N sulfuric acid, using a 10-cubic-centimeter microburet, until the color changes from green to faint purple. The 0.2 N sulfuric acid is standardized by pipetting a 10-cubic-centimeter aliquot of standard ammonium chloride solution into the distillation flask. Water is added and the steps are repeated from the beginning of the paragraph. The percentage of nitrogen is calculated as follows:

$$\text{Percent N} = \frac{\text{cm}^3 \text{H}_2\text{SO}_4 \times \text{Normality} \times 1.4007}{\text{Grams UN}}$$

APPENDIX D

INERT-GAS FUSION METHOD FOR OXYGEN

Apparatus and Materials

A LECO Corporation induction furnace Model 537 and a chromatographic gas analyzer Model 589-400 are used for the oxygen determination. The analyzer is calibrated by adding CO₂ through a gas sampling valve of known volume. Tin capsules containing weighed amounts of potassium acid phthalate could also be used for calibration. Samples are enclosed in platinum capsules made from 6.35-millimeter-inside-diameter by 0.10-millimeter-wall tubing cut into 22-millimeter lengths. Each capsule weighs about 1 gram. Platinum used for the bath is made from 0.22-millimeter commercial-grade wire cut into 12-millimeter lengths. Temperature measurements are made with an optical pyrometer. Graphite crucibles are Ultra Carbon type 810204.

Preparation of Sample

Samples of 0.25 to 0.5 gram are weighed and sealed in platinum capsules in an argon-gas-filled glove box. Each capsule is placed in a glass vial and closed with a plastic screw cap. Each vial is then placed in a larger glass vial which is capped. The samples are stored in the glove box until time for analysis. In any event, all samples should be analyzed within 24 hours after preparation.

Preparation of Apparatus

A graphite crucible is supported in the silica furnace thimble with carbon black insulation and outgassed at 2400°C for at least 1 hour in the inert-gas fusion furnace. Helium used for the furnace carrier gas is purified by passing it through molecular sieve 5-A at liquid-nitrogen temperature. The helium is then passed through hot titanium chips (600°C) before it enters the induction furnace.

After the crucible is outgassed, the furnace power is reduced until the crucible temperature is approximately 1700°C. Platinum wire for the bath is added, and the crucible temperature is reset to 2100°C. The amount of platinum added is 12 grams, a quantity which, together with the 1-gram sample container, is enough to maintain a 10:1 platinum-to-sample ratio.

Procedure

When the bath has been outgassed for at least 30 minutes, the carrier gas flow rate is set to 1000 cubic centimeters per minute. A number of 3-minute blanks are determined. Blanks are run until they are constant and equivalent to 2 to 3 micrograms of oxygen per minute. Two or three blank sample capsules are analyzed. Each sample is then analyzed, using a 3- to 5-minute extraction time. Crucible blanks are determined between each sample to check for completeness of oxygen extraction.

The CO extracted from the sample is oxidized to CO₂ by CuO at 400° C and adsorbed on molecular sieve 5-A. At the end of the 3-minute extraction time the molecular sieve trap is heated to 350° C. The adsorbed CO₂ is swept through a silica gel column and over a thermal conductivity detector to measure its quantity. The signal from the thermal conductivity detector is measured with either a digital integrator or a strip-chart recorder.

APPENDIX E

COMBUSTION-CHROMATOGRAPHIC METHOD FOR CARBON

Apparatus and Materials

The apparatus and materials used for the carbon determination include a LECO Corporation model 521-100 induction furnace, a LECO model 589-400 chromatographic gas analyzer, LECO 528-35 induction furnace crucibles, a LECO 501-317 low-carbon iron chip accelerator, and reagent-grade wire-form copper oxide. The crucibles and copper oxide should be ignited in oxygen at 1000^o C and then stored in a closed container until used.

Oxygen used to burn the samples may be purified by passing it through CuO heated to 400^o C and then through molecular sieve 5-A to remove CO₂ and H₂O. A combination of Ascarite and magnesium perchlorate may be substituted for the molecular sieve if desired. Helium for the gas analyzer is purified by passing it through molecular sieve 13-X and activated charcoal at room temperature.

Procedure

To each crucible, 1.0 gram of low-carbon iron plus 0.5 gram of CuO is added. Samples of uranium mononitride weighing between 0.3 and 0.5 gram are added on top of the iron and CuO. Each sample is placed in the induction furnace and ignited for 2 minutes at an oxygen flow rate of 1000 cubic centimeters per minute and pressure of 6.9 newtons per square centimeter (10 psi). The oxygen and combustion products are swept through a glass-wool-filled dust trap, through a CuO catalyst furnace to convert any CO to CO₂, and then through a magnesium perchlorate drying tube and into the gas analyzer. The gases next go through a trap containing molecular sieve 5-A which adsorbs CO₂ from the gas stream. At the completion of the 2-minute burn, a solenoid valve isolates the molecular sieve trap from the furnace and connects it to the helium carrier gas of the analyzer. Simultaneously, the trap is heated to 350^o C to release CO₂ from the molecular sieve. The helium carrier gas sweeps the CO₂ through a silica-gel-filled chromatographic column and then through a thermal conductivity cell. The signal from the thermal conductivity cell can be measured with either a digital integrator or a strip-chart recorder. Standardization of the analyzer can be done by injecting CO₂ gas at known pressure and temperature by using gas sampling valves or syringes. Tin capsules containing known amounts of potassium acid phthalate could also be used to calibrate the analyzer.

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