AEC RESEARCH AND DEVELOPMENT REPORT

SPECTROCHEMICAL DETERMINATION OF
IMPURITIES IN TUNGSTEN

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For the Atomic Energy Commission
Under U.S. Government Contract W7405 eng 26

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Printed in the United States of America. Available from Clearinghouse for Federal
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U.S. Department of Commerce, Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

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H.C. \$ 3.00; MN .65

Date of Issue: July 5, 1967

Report Number: K-1683

Subject Category: CHEMISTRY

SPECTROCHEMICAL DETERMINATION OF
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Technical Division

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A B S T R A C T

Twelve spectrochemical procedures have been developed for the determination of impurities in tungsten. These procedures include a direct burn method for calcium, eight carrier distillation procedures for common metals, the cupferron group separation, the platinum group separation by zinc reduction and separation of the rare earth elements using an ammonia precipitation. Sixty-one elements are measurable; fifty-six of the elements are determinable in the range of 0.1 to 3 ppm.

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SPECTROCHEMICAL DETERMINATION OF
IMPURITIES IN TUNGSTEN

CONTENTS

INTRODUCTION	7
SUMMARY	7
OBJECTIVES AND RESULTS	8
BIBLIOGRAPHY	10
APPENDICES	
A. Spectrochemical Determination of Calcium in Tungsten Powder by the Direct Burn Technique	11
B. Spectrochemical Determination of the Carrier Group Elements in Tungsten Powder	15
C. Spectrochemical Determination of the Cupferron Group Elements in Tungsten Powder	25
D. Spectrochemical Determination of the Platinum Group Elements in Tungsten Powder using the Zinc Reduction Separation	31
E. Spectrochemical Determination of the Rare Earth Elements in Tungsten Powder	37

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SPECTROCHEMICAL DETERMINATION OF IMPURITIES IN TUNGSTEN

Increased applications of tungsten in electronic systems, aircraft, missiles and space work have increased the need for analytical methods capable of high sensitivity and broad coverage for contaminant elements in this metal. Optical-emission spectrochemical methods were investigated because many elements were potentially determinable simultaneously at the parts-per-million level, with acceptable precision and accuracy.

Methods for the measurement of impurities in uranium have been developed over many years of experience by the Atomic Energy Commission and its contractors (1,2,3). The Oak Ridge Gaseous Diffusion Plant has been active in this field and has developed a number of methods to monitor material purity specifications. The Oak Ridge Gaseous Diffusion Plant has also developed a group of spectrographic and wet chemical procedures for the determination of impurities in ultra-high purity tungsten-uranium dioxide mixtures (4).

Although several references have appeared in the literature in recent years for the determination of impurities in tungsten, none provided the extent of element coverage attained for uranium and tungsten-uranium dioxide mixtures. The method of Veleker and Dyck (5) permits the determination of only 13 elements in tungsten metal powder and in tungstic oxide. The fine article of Gabler and Peterson of the Bureau of Mines (6), which appeared near the completion of this work, covers the investigation and modification of the published methods of Peterson and Chaney (7), Gentry and Mitchell (8) and Meister, et al (9). They suggest three preferred methods of analysis: a germanium carrier distillation procedure applicable to the determination of 13 elements in tungsten powder; a silver chloride carrier distillation procedure for the determination of 24 elements in tungstic oxide; and a sustaining arc method for the determination of 25 elements in tungstic oxide. The combination of their methods provides a coverage of 26 different elements; no attempts were made in the study to investigate preconcentration methods for the analysis of other elements. Gordon (10,11) has used an argon atmosphere at reduced pressure in special equipment to investigate lower limits of detection for at least 17 elements by the carrier distillation technique.

SUMMARY

Twelve spectrochemical procedures are presented for the determination of impurities in high purity tungsten. Sixty-one metallic elements, including the rare earth elements, are included in the coverage. The total of the lower limits of detection in tungsten by these procedures is about 95 ppm.

OBJECTIVES AND RESULTS

The objective of the development program of the present authors was to provide procedures for determining impurities in high purity tungsten, with lower limits of detection and extent of element coverage similar to those attained in the analysis of high purity uranium materials and tungsten-uranium dioxide mixtures. The element groupings are similar to those employed in the other programs; however, the carrier distillation techniques involve the selection of different carriers than previously, due to the characteristics of excitation with the new tungsten matrix. Methods of preconcentration of impurities, with the tungsten matrix, are similar to earlier methods for the platinum and cupferron groups; the separation necessary for the rare earths is newly devised, and is simpler because of the absence of uranium.

The program successfully achieved, and surpassed, its goals. Fifty-six of the elements are determinable in the range of 0.1 to 3 ppm. The total of the lower limits of detection achieved for the coverage of 61 elements is about 95 ppm, as shown in table I, which compares with about 150 ppm for 64 elements determined in U_3O_8 and 130 ppm for 61 elements in tungsten-uranium dioxide mixtures (4). This greater sensitivity is attributed primarily to better detection limits for As, Ba, Co, Ga, Ir, P, Rb, Ru, Ta and Th in the pure tungsten.

The spectrum of tungsten is very complex and the possibility of tungsten line interference with the impurity element lines was a constant problem. The tungsten spectrum can be suppressed through the formation of tungsten carbide. Graphite or carbon powder is often added to the spectrographic charges to hasten the formation of the tungsten carbide (6). The carrier group measurement requires eight procedures to obtain 39 elements. However, with improved excitation equipment for the Jarrell-Ash spectrograph, this could be reduced to six procedures. A set of working procedures, which can be applied in other laboratories, is provided in the Appendices of this report. Specific problems are discussed and pertinent literature references are presented with each procedure, rather than in a separate part of the report, for the convenience of the reader and the user of the procedures.

TABLE I

SPECTROCHEMICAL SENSITIVITIES ACHIEVED FOR
IMPURITIES IN TUNGSTEN

<u>Element</u>	<u>Limit of Detection, (ppm)</u>	<u>Element</u>	<u>Limit of Detection, (ppm)</u>	<u>Element</u>	<u>Limit of Detection, (ppm)</u>
Ag	1	K	1	Ti	1
Al	1	Li	1	Tl	1
As	3	Mg	1	V	1
Au	1	Mn	1	Zn	15
B	1	Mo	1	Zr	1
Ba	1	Na	5	<u>Rare Earths</u>	
Be	0.1	Nb	1	Ce	1
Bi	1	Ni	1	Dy	0.5
Ca	1	P	5	Er	0.5
Cd	1	Pb	1	Eu	0.5
Co	3	Pd	1	Gd	0.5
Cr	3	Pt	1	Ho	0.5
Cs	10	Rb	5	La	0.5
Cu	0.1	Rh	1	Lu	0.5
Fe	1	Ru	1	Nd	0.5
Ga	1	Sb	1	Pr	0.5
Ge	1	Si	1	Sm	0.5
Hf	1	Sn	1	Tb	0.5
Hg	2	Sr	1	Tm	0.5
In	1	Ta	1	Yb	0.5
Ir	1	Th	0.5		

BIBLIOGRAPHY

- (1) Rodden, C. J., Editor, et al., Analytical Chemistry of the Manhattan Project, NNES, Division VIII, Vol. 1, 1st Ed., New York, McGraw-Hill, 1950. UNCLASSIFIED.
- (2) Rodden, C. J., Current Procedures for the Analysis of UO_3 , UF_4 , and UF_6 , USAEC, Technical Information Service, February 1956 (TID-7003). UNCLASSIFIED.
- (3) Jones, R. J., Editor, Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle, USAEC, Division of Technical Information, 1963 (TID-7029). UNCLASSIFIED.
- (4) Weber, C. W. and Kwasnoski, T., "Unpublished Report," February 19, 1965.
- (5) Methods for Emission Spectrochemical Analysis, "Analysis of Tungsten by Powder - A.C. and D.C. Arc Techniques," Fourth Edition, American Society for Testing and Materials, Philadelphia, Pa. (1964).
- (6) Gabler, R. C., Jr. and Peterson, M. J., Spectrochemical Analysis of Tungsten, U. S. Department of the Interior, Bureau of Mines, 1965 (Report of Investigation No. 6632).
- (7) Peterson, M. J. and Chaney, C. L., Semiquantitative Spectrographic Analysis of Tungsten, U. S. Department of the Interior, Bureau of Mines (1961) (Report of Investigation No. 5903).
- (8) Gentry, C. H. R. and Mitchell, G. P., "Spectrochemical Analysis of Tungsten," Metallurgia, 46, 1952, pp. 47-51.
- (9) Meister, I., Gritz, E. E. and Ellis, T. A., Spectrographic Analyses of Trace Impurities in Tungsten, Parts I and II. Phase II - Final Report on Manufacturing of Tungsten and Tungsten Alloys for Rocket Nozzles, Westinghouse Electric Corporation, Bloomfield, N. J., 1961. UNCLASSIFIED.
- (10) Gordon, W. A., Use of Temperature Buffered Argon Arc in Spectrographic Trace Analysis, NASA, Lewis Research Center, Cleveland, Ohio, January 1965 (NASA TN D-2598). UNCLASSIFIED.
- (11) Gordon, W. A., NASA, Lewis Research Center, Private Communication, February, 1965.

APPENDIX A

SPECTROCHEMICAL DETERMINATION OF CALCIUM IN TUNGSTEN
POWDER BY THE DIRECT BURN TECHNIQUE

Scope and Sensitivity

This method is applicable to the determination of low levels of calcium in tungsten powder. Although the method was developed particularly for relatively pure materials, concentrations of calcium as high as 1000 ppm can be measured by regulating the amount of emitted light which reaches the photographic plate.

The limit of detection (estimated visually) is 1 ppm of calcium in the tungsten powder.

Summary of the Method

Forty milligrams of the powdered tungsten metal sample is placed in a graphite electrode, graphite powder is added and excited with the direct current arc. The resulting spectrum on the photographic plate is compared visually with standard spectra to obtain the calcium determination.

Precision

The 95% confidence limits of a single measurement are +100 and -50% of the value, estimated visually.

Apparatus and Reagents

Mortar, boron carbide.

Plastic vials, 1/2 inch diameter x 1 inch long.

Plexiglas grinding balls, 3/8 inch diameter.

Mixer-Mill, sample shaker.

Electrodes, Graphite:

Lower: 3/16 inch undercut, Ultra Carbon type 4880 or equivalent.

Upper: 1/8 inch rod, 1-1/2 to 2 inches long, pointed with a pencil sharpener.

Graphite powder, National Carbon Company SP-2 or equivalent.

Spectrograph, Jarrell-Ash (Wadsworth).

Power Source, direct current (motor generator set).

Photographic plates, Eastman Kodak Spectrum Analysis No. 1.

Filter, plate glass with mount.

Rotating sector.

Comparator - microphotometer, Jarrell-Ash or equivalent.

Developer, Eastman Kodak D-19.

Acid short stop, Eastman Kodak SB-1.

Photographic fixer, Eastman Kodak F-5.

Sample Preparation Procedure

1. Blend the sample, using a plastic vial, ball pestles and Mixer Mill.
2. Weigh three 40 mg charges into separate electrodes.
3. Pack the sample into the bottom of the cavity by holding the electrode with a pair of forceps and tapping it lightly on the bench top.
4. Add 20 mg graphite to the top of each charge and pack by holding the electrode with a pair of forceps and tapping again on the bench top.

Spectrograph Operation Procedure

1. Position the plate holder on the Jarrell-Ash spectrograph and make appropriate adjustments to operate the spectrograph as follows:

Arc Stand Position	50 cm from slit.
Slit Height	3 mm
Slit Width	30 microns
Collimating Mirror Mask	20 mm x 135 mm
Filter	Plate glass
Automatic Feed (for plate)	On and set for 3 mm automatic rackdown
Timer	On and set for 90 seconds
Rack Number	At 10
Wave Length Setting	8500 Angstroms at center of plate holder.

Sector

Rotating - 10% transmission

Excitation

5 amps dc - 10 seconds

7 amps dc - 10 seconds

11 amps dc - 70 seconds

2. Wipe off the electrode clamps; insert the electrodes and adjust the gap distance to 4 millimeters by adjusting the projected image of the gap on the target screen.
3. Turn on the dc arc, adjust source to 5 amps, and excite for 10 seconds, increase to 7 amps for 10 seconds, and increase to 11 amps for an additional 70 seconds.
4. Maintain 4 millimeter gap distance throughout the exposure by adjusting the electrodes when necessary.
5. Repeat the exposure cycle for the next sample.

Photographic Plate Handling Procedure

1. With only the darkroom safe light on, develop the plate for 2 minutes at 68°F.
2. Place the developed plate in the short stop bath for 20 seconds.
3. Place the plate in the fixing bath for 2 minutes.
4. Wash the plate for 2 minutes.
5. Rinse the plate with distilled water, remove the excess water and dry the plate on a plate dryer.

Photographic Plate Reading Procedure

1. Using the comparator-microphotometer, visually compare the density of the calcium lines with those on a standard plate to estimate the concentration in the sample.
2. The following lines are used in the identification and estimation of calcium:

<u>Element</u>	<u>Wave Length, Angstroms</u>
Ca	3933.67
Ca	3968.47

Discussion

Calcium is the only element which could be measured to the desired sensitivity using the direct burn approach. The calcium lines have no tungsten interference and the line intensities are such that the background can be filtered and still yield adequate sensitivity for calcium measurement.

APPENDIX B

SPECTROCHEMICAL DETERMINATION OF THE CARRIER
GROUP ELEMENTS IN TUNGSTEN POWDER

Scope and Sensitivity

This method is applicable as a general purpose procedure for the determination of 39 of the common metallic impurities in tungsten metal powder. Since the method was developed particularly for relatively pure materials, modifications may be necessary if applied to samples containing more than 1000 ppm total impurities.

The elemental coverage and limits of detection (estimated visually) for the procedure are listed in table II.

TABLE II

SPECTROCHEMICAL SENSITIVITIES FOR THE CARRIER
GROUP ELEMENTS IN TUNGSTEN

<u>Element</u>	<u>Limit of Detection (ppm)</u>	<u>Element</u>	<u>Limit of Detection (ppm)</u>
Ag	1	Mg	1
Al	1	Mn	1
As	3	Mo	10
Au	1	Na	5
B	1	Nb	20
Ba	1	Ni	1
Be	0.1	P	5
Bi	1	Pb	1
Cd	1	Pd	1
Co	3	Rb	5
Cr	3	Sb	1
Cs	10	Si	1
Cu	0.1	Sn	1
Fe	1	Sr	1
Ga	1	Ti	1
Ge	1	Tl	1
Hg	2	V	5
In	1	Zn	15
K	1	Zr	2
Li	1		

Summary of the Method

The sample in the form of tungstic oxide (WO_3) or tungsten metal powder is mixed with a carrier (1,2), placed in the crater of a graphite electrode, and excited in a dc or ac arc. The spectrum, recorded photographically, is compared visually with standard spectra.

Precision

The estimated 95% confidence limits of a single measurement are +100% and -50% of the value, at concentrations near the limit of detection.

Apparatus and Reagents

Mortar, tungsten carbide (for standards preparation).

Mixer Mill.

Wig-L-Bug, sample shaker.

Balance, Roller - Smith.

Plastic vials, 1/2 inch diameter x 1 inch long.

Plexiglas grinding balls, 3/8 inch diameter.

Platinum spatula.

Platinum funnel.

Electrodes, graphite:

Lower: 0.242 inch rod, with a cup 0.156 inch in diameter and 0.2812 inch deep. National Carbon SPK L-4224 or equivalent.

0.242 inch rod with a cup 0.156 inch in diameter and 0.2812 inch deep, National Carbon AGKSP L-4024 or equivalent, fitted with a boiler cap 0.305 inch OD, 0.2425 inch ID with a vent hole 0.038 inch diameter, National Carbon SPK L-3715 or equivalent.

0.180 inch rod, 1.500 inch long, with a cup 0.150 inch in diameter and 0.276 inch deep. National Carbon SP 9065 or equivalent.

3/16 inch undercut, Ultra Carbon type 4880 or equivalent.

Upper: 1/8 inch rod, 1-1/2 to 2 inches long, pointed with a pencil sharpener.

1/8 inch rod, 1-1/2 to 2 inches long, flat-topped.

3/16 inch diameter rod with 120° included angle tip.

Vent-forming tool (3), see figure 1.

Packing tool - 1/8 inch graphite rod, 1-2 inches long with flat ends.

Spectrograph, Jarrell-Ash (Wadsworth).

Spectrograph, Bausch and Lomb (Littrow).

Power source, direct current (Jarrell-Ash Varisource or motor generator set).

Filter, Corning No. 3384.

Photographic plates: Eastman Kodak Spectrum Analysis No. 1, Eastman Kodak type 1-N and Eastman Kodak Spectrum Analysis No. 3.

Plate developing and drying equipment.

Developer, Eastman Kodak D-19.

Acid short stop, Eastman Kodak SB-1.

Photographic fixer, Eastman Kodak F-5.

Microphotometer, Jarrell-Ash or equivalent.

Comparator, Applied Research Laboratories or equivalent.

Graphite powder, National Carbon Company SP-2 or equivalent.

Silver chloride, spectrographic grade.

Sodium chloride, spectrographic grade.

Sodium carbonate, spectrographic grade.

Carbon powder, mesh 325, Ultra Carbon type UCP 3, or equivalent.

Graphite - 0.5% germanium oxide mixture. Mix 995 mg graphite with 5 mg germanium oxide in a plastic vial on the Mixer Mill.

Sample Preparation Procedure

1. Convert tungsten metal to WO_3 by igniting in a muffle furnace at 700°C. for one hour. Weigh 0.020 g of silver chloride, 0.180 g of the WO_3 (sample) and 0.200 g of graphite successively into a plastic grinding vial. Add a plastic grinding ball to the vial and grind together on a Wig-L-Bug. This mixture is used in the determination of elements in Procedure A (see tables III and IV).

2. Weigh 200 mg of tungstic oxide and 200 mg of the graphite-germanium oxide mixture (2) into a plastic vial. Grind together on a Wig-L-Bug, using plastic grinding balls in the vial. This mixture is used in the determination of elements in Procedure G (see tables III and IV).
3. Blend the tungsten powder and prepare a mixture (4,5) of 0.105 g NaCl, 1.095 g tungsten powder and 0.300 g graphite (weighed successively into a plastic grinding vial). Grind together on a Wig-L-Bug using plastic grinding balls in the vial. This mixture is used in the determination of elements in Procedures B, C, D and E (see tables III and IV).
4. Blend the tungsten powder and prepare a mixture (6) of 0.025 g Na_2CO_3 , 0.425 g tungsten powder and 0.050 g carbon powder (weighed successively into a plastic grinding vial). Grind together on a Wig-L-Bug using plastic grinding balls in the vial. This mixture is used in the determination of elements in Procedure F (see tables III and IV).
5. Blend the tungsten powder and prepare a mixture of 0.200 g graphite powder and 1.000 g of tungsten powder. Grind together on a Mixer-Mill using plastic vial and grinding balls. This mixture is used in the determination of elements in procedure H (see tables III and IV).
6. Weigh three 0.100 g charges of the appropriate mixture from steps 1, 3 and 4 for procedures A, B, C, D, E, and F (tables III and IV).
7. Weigh three 0.050 g charges of the mixture from step 2 for excitation procedure G (tables III and IV).
8. Weigh three 0.020 g charges of the mixture from step 5 for excitation procedure H (tables III and IV).
9. Using a platinum funnel, transfer the charges to appropriate graphite electrodes.
10. Pack the sample into the bottom of the cavity by holding the electrode with a pair of forceps and tapping it briskly on the bench top.
11. Pack the charge using the appropriate packing or vent-forming tool (table III).

Spectrograph Operation Procedure

1. To cover the complete range of elements listed, this procedure requires a series of exposures on two spectrographs using the 8 sets of conditions shown in table III.
2. Align the electrodes and adjust the gap width to 4 mm.
3. Adjust the appropriate spectrograph to the conditions given in table III, and expose the sample for the time indicated.

4. Maintain the 4 millimeter gap distance throughout the exposure by adjusting the electrodes when necessary.
5. At the completion of the exposure, remove the electrodes and discard.
6. Repeat with a second and third electrode to give triplicate exposures.

Photographic Plate Handling Procedure

1. With only the darkroom safe light on, develop the S.A. No. 1 plates in procedures A, C, D, E, and G for two minutes at 68°F.
2. Place the developed plates in the short stop bath for 20 seconds.
3. Place the plates in the fixing bath for two minutes.
4. Wash the plates for two minutes.
5. Rinse the plates with distilled water, remove the excess water with a cellulose sponge and dry the plates on a plate dryer.
6. Develop the S.A. No. 3 plate in procedure F for 3 minutes at 68°F., short stop for 20 seconds, and fix for 3 minutes.
7. Develop the 1-N plates in procedures B and H in total darkness for 3 minutes, short stop for 20 seconds, and fix for 3 minutes.

Photographic Plate Reading Procedure

Use the Applied Research Laboratories Comparator (or equivalent) and visually compare the density of the lines with those on a standard plate to estimate the concentration of the elements sought in the sample. Table IV lists the wavelengths used for the various elements.

Discussion

All tungsten samples are arced as fine powders of the oxide or metal. Eight methods of sample preparation and excitation are required to obtain high sensitivity. If the sample is received in a form other than a fine metal or oxide powder, the sample should be oxidized in air at 700°C. and a portion reduced in hydrogen at 900°C. for one hour, in order to convert the sample to the proper form for analysis. Losses of volatile elements (e.g. arsenic and mercury) may occur during oxidation while other elements (e.g. lead, copper, and tin) may be partially lost during reduction (2,7); therefore, caution should be observed in reporting elements of these types in samples which have been oxidized and reduced.

Elements in procedure A are determined using tungstic oxide; this procedure was developed for samples received as tungstic oxide or converted to the oxide. In general, however, the carrier procedures for tungsten metal powder give better matrix suppression than those for tungstic oxide.

Procedures C, D, and E use the same carrier and differ only by the spectrographic setting or spectrograph used. If a 15 ampere dc current were available for excitation of samples on the Jarrell-Ash spectrograph, it would be possible to combine these three procedures into one procedure and obtain satisfactory sensitivities for all the elements in these groups.

Providing a vent hole in the sample charge with the vent-forming tool permits carrier gases to escape and minimizes tungsten excitation.

In selecting wavelengths to use in estimating element concentrations, close attention should be given to tungsten lines which may interfere.

References

- (1) Scribner, B. F. and Mullin, H. R., "Carrier Distillation Method for Spectrographic Analysis and its Applications to the Analysis of Uranium-Base Materials," Journal of Research, NBS, 37, 379-389 (1946).
- (2) Gabler, R. C., Jr. and Peterson, M. J., Spectrochemical Analysis of Tungsten, United States Department of Interior, Bureau of Mines, 1965, Report of Investigations No. 6632.
- (3) Leslie, E. H., Note on Improvements in Spectrochemical Techniques, Carbide and Carbon Chemical Corporation, K-25 Plant, December 28, 1948 (K-325). UNCLASSIFIED.
- (4) Cotterill, J. C., The Spectrographic Analysis of Uranium and Uranium Compounds by the Carrier Distillation Technique, Chemistry Division, Atomic Energy Research Establishment, Harwell, Berkshire, 1963 (AERE-AM 94).
- (5) Notkina, M. A., Solodoonik, S. M., Barnova, L. L., Lushina, V. K., and Romantseva, T. I., Increased Sensitivity in the Detection of Impurities in High Purity Metals, State Research and Design Institute for the Rarer-Metals Industry, Translated from Zavodskaya Laboratoriya, Vol. 28, No. 2, pp. 176-177, February 1962.
- (6) Zaidel, A. N., Kaliteevskii, N. I., Lipis, L. V., and Chaika, M. P., Emission Spectrum Analysis of Atomic Materials, Book I. (Translated from a publication of the State Publishing House of Physicomathematical Literature, Moscow, U.S.S.R., 1960, USAEC, Division of Technical Information, AEC-tr-5745, pp. 343-349).
- (7) Methods for Emission Spectrochemical Analysis, E-2 SM 8-18, Fourth Edition, American Society for Testing and Materials, 1964, pp. 559-565.

TABLE III

SPECTROGRAPH OPERATING CONDITIONS FOR VARIOUS CARRIER PROCEDURES

Procedure	A(WO ₃)	B (W)	C (W)	D (W)	E (W)	F (W)	G(WO ₃)	H (W)
Elements Sought	See Table IV	See Table IV	See Table IV	See Table IV	See Table IV	See Table IV	See Table IV	See Table IV
Spectrograph	Jarrell-Ash	B&L Littrow	B&L Littrow	B&L Littrow	Jarrell-Ash	B&L Littrow	B&L Littrow	Jarrell-Ash
Wavelength Setting or Range	5750 Angstroms at center of plateholder	3500-8000 Å	2500-3500 Å	2250-2900 Å	5750 Angstroms at center of plateholder	2250-2900 Å	2500-3500 Å	6800 Angstroms at center of plateholder
Current	11 amps dc	15 amps dc	15 amps dc	15 amps dc	11 amps dc	30 amps dc	5 amps ac	7 amps dc
Preburn	None	None	None	None	None	None	None	None
Exposure	120 sec	75 sec	75 sec	75 sec	120 sec	45 sec	30 sec	60 sec
Photographic Plate	SA #1	1-N	SA #1	SA #1	SA #1	SA #3	SA #1	1-N
Carrier	AgCl	NaCl	NaCl	NaCl	NaCl	Na ₂ CO ₃	Graphite - germanium oxide mix- ture	Graphite
External Optics								
Arc Stand Position	50 cm from slit	29 cm from slit	29 cm from slit	29 cm from slit	50 cm from slit	29 cm from slit	29 cm from slit	50 cm from slit
Condensing Lens Type	100 mm cylindrical				100 mm cylindrical			100 mm cylindrical
Step Filter	35%	10%	35%	35%	35%	35%	10%	20%
Filter								Corning 3384
Slit Cover Lens Type	45 cm cylindrical	25 cm spherical	25 cm spherical	25 cm spherical	45 cm cylindrical	25 cm spherical	25 cm spherical	45 cm cylindrical
Slit Width	30 microns	25 microns	25 microns	25 microns	30 microns	25 microns	25 microns	30 microns
Slit Height	3 mm	3 mm	3 mm	3 mm	3 mm	3 mm	3 mm	3 mm
Collimating Mirror								
Mask	20 mm x 135 mm	Closed	Closed	Closed	20 mm x 135 mm	Closed	Closed	20 mm x 135 mm
Electrodes								
Anode	National Carbon SP-9065	National Carbon SPK L-4224	National Carbon SPK L-4224	National Carbon SPK L-4224	National Carbon SPK L-4224	National Carbon AGKSP L-4024 SPK L-3715	3/16" undercut Ultra Carbon type 4880	3/16" undercut Ultra Carbon type 4880
Cathode	1/8" pointed tip	1/8" pointed tip	1/8" pointed tip	1/8" pointed tip	1/8" pointed tip	1/8" flat	3/16" rod with 120° included tip	1/8" pointed tip
Arc Gap	4 mm	4 mm	4 mm	4 mm	4 mm	4 mm	4 mm	4 mm
Electrode Charge	100 mg	100 mg	100 mg	100 mg	100 mg	100 mg	50 mg	20 mg
Packing Tool	Flat 1/8" Rod	Vent-forming tool	Vent-forming tool	Vent-forming tool	Vent-forming tool	None	None	None

TABLE IV

22

TABLE IV (Cont'd)

WAVELENGTHS USED FOR ELEMENTS IN CARRIER PROCEDURES
(VALUES IN ANGSTROMS)

Procedure E			Procedure F			Procedure G			Procedure H		
Element	Limit of Detection, (ppm)	Suggested Wave- lengths	Element	Limit of Detection, (ppm)	Suggested Wave- lengths	Element	Limit of Detection, (ppm)	Suggested Wave- lengths	Element	Limit of Detection, (ppm)	Suggested Wave- lengths
Au	1	2427.95 2675.95	As	3	2288.12 2349.84 2780.20	Zn	15	3302.6 3345.6	Na	5	5889.95 5895.93
Ga	1	2874.24 2943.64	Hg	20	2536.5	Ge (Internal Std.)		2740.43			
Ge	1	2651.18 2709.63	P	5	2534.01 2535.65 2553.28 2554.93						
In	1	2710.26 3039.36									
Pd	1	3404.58									
Tl	50	2918.32

Figure 1
VENT-FORMING TOOL

APPENDIX C

SPECTROCHEMICAL DETERMINATION OF THE CUPFERRON
GROUP ELEMENTS IN TUNGSTEN POWDER

Scope and Sensitivity

This method is applicable to the determination of those metallic impurities in tungsten powder which can be precipitated as cupferrides in the presence of tartaric acid. Tungsten, which normally forms the cupferride under the acidity conditions of this precipitation, remains in solution as the tartaric acid complex. Since the method was developed for relatively pure materials, concentrations of these elements in excess of 100 ppm would probably require modifications in the method.

The elemental coverage and limits of detection (estimated visually) for this procedure are listed in table V.

TABLE V

SPECTROCHEMICAL SENSITIVITIES FOR THE CUPFERRON
GROUP ELEMENTS IN TUNGSTEN POWDER

<u>Element</u>	<u>Limit of Detection (ppm)</u>	<u>Element</u>	<u>Limit of Detection (ppm)</u>
Ga	1	Ti	1
Hf	1	V	1
Mo	1	Zr	1
Nb	1		
Ta	1		

Summary of the Method

Gallium, hafnium, molybdenum, niobium, tantalum, titanium, vanadium and zirconium are separated from the tungsten solution by extraction as the cupferrides into chloroform (1,2). After evaporation of the solvent and ignition of the residue, the ignited residue is dissolved in a mixture of hydrochloric-hydrofluoric acids, palladium is added, and the solution is sparked by the rotating disk technique. The resulting spectrum, recorded photographically, is compared visually with standard spectra to obtain a measurement of the cupferron elements. The palladium additive serves as a reference. For more precise determination, the intensities of the analytical lines are measured with a microphotometer, the palladium serving as an internal standard.

Precision

The estimated 95% confidence limits of a single measurement (by visual comparison) are +100% and -50% of the value, at concentrations near the limit of detection.

Apparatus and Reagents

Power source, for high voltage spark, controlled by an air interrupter.

Rotating disk assembly, consisting of a rotating disk electrode holder and drive. The disk is rotated at a selected constant speed of from 2 to 6 rpm.

Spectrograph, Bausch and Lomb, large Littrow mount, or equivalent.

Comparator-microphotometer, Jarrell-Ash, or equivalent.

Teflon dish, 0.8 ml capacity, 5/32 inch deep, to hold sample solution during sparking.

Hot plate.

Muffle furnace.

pH meter.

Ice bath.

Separatory funnel, 500 ml capacity.

Platinum dish, 300 ml capacity.

Electrodes, graphite:

Lower: high purity rod, 1/8 inch diameter, blunt end.

Upper: high purity disk, 1/2 inch diameter, 1/8 inch thick, with a 1/8 inch hole through the center. Ultra Carbon type 106 or equivalent.

Photographic plates, Eastman Kodak Spectrum Analysis No. 1, or equivalent.

Developer, Eastman Kodak D-19.

Acid short stop, Eastman Kodak SB-1.

Photographic fixer, Eastman Kodak F-5.

Palladium Solution, 0.20 mg Pd/ml:

Dissolve 0.17 g of palladium chloride in a minimum amount of concentrated hydrochloric acid and dilute to 500 ml volume with water.

Cupferron solution, 8% (wt/vol):

Dissolve 80 g of cupferron in water and dilute to 1 liter.

Chloroform, ACS reagent grade.

Nitric acid, conc. (16 M).

Sulfuric acid, concentrated (18 M), 9 M, 1 M.

Hydrofluoric acid, 48%.

Sodium hydroxide, 20%.

Hydrochloric acid, concentrated (12 M).

Tartaric acid powder, ACS reagent grade.

Separation Procedure

1. Add 15 ml of 48% hydrofluoric acid to a 5 gram sample of tungsten in a platinum dish (3).
2. Add concentrated (16 M) HNO_3 dropwise until the tungsten is dissolved.
3. Place on hot plate and evaporate very carefully to dryness.
4. Cool the sample, add 10 ml of concentrated sulfuric acid and evaporate to dryness on a hot plate.
5. Cool and dissolve the residue by adding a minimum quantity of 20% sodium hydroxide. Place on a hot plate, if necessary, to dissolve the residue.
6. Transfer the sample to a 400 ml beaker and dilute to 200 ml.
7. Add 50 grams of tartaric acid and heat on a hot plate until the tartaric acid is dissolved.
8. Cool the solution and adjust to $\text{pH } 2 \pm 0.1$ with 9 M sulfuric acid.
9. Transfer the sample to a 500 ml separatory funnel and dilute to 250 ml.
10. Cool the sample in an ice bath to about 5°C .
11. Add 5 ml of 8% cupferron solution to precipitate the cupferrides; shake the mixture well and place in the ice bath for five minutes.
12. Add 20 ml of chloroform to the separatory funnel and shake until most of the precipitate dissolves. (The precipitate may not dissolve completely on the first extraction.) Allow the phases to separate.

13. Separate the chloroform phase, catching it in a separatory funnel.
14. Repeat the extraction with several 20 ml quantities of chloroform until all the cupferrides are removed. Combine the collected organic phases.
15. Wash the combined extracts twice with 40 ml of cold 1 M sulfuric acid. Allow the phases to separate and discard the washings.
16. Cool the aqueous solution from step 14 in an ice bath to 5°C., add 5 ml of 8% cupferron solution, shake well, and cool for an additional 5 minutes.
17. Repeat steps 12 through 15 and combine the chloroform extract with the original chloroform extract from step 15.
18. Transfer the combined chloroform extracts to a platinum dish, place under a hood, and evaporate to dryness at room temperature.
19. Transfer the platinum dish to a cold furnace set for a maximum of 500°C.; heat gradually to the maximum temperature, and then ignite until all the carbon has been destroyed.
20. Dissolve the residue in a mixture of 5 ml of concentrated hydrochloric acid and 1 ml of 48% hydrofluoric acid. Add 2 ml of palladium solution (400 micrograms of palladium) as a reference or internal standard. Evaporate the mixture to 0.5 ml $\pm$ 0.2 ml volume for spectrographic analysis.

Spectrograph Operation Procedure

1. Position the plate holder containing a photographic plate on the Littrow spectrograph.
2. Place the 1/8 inch counter electrode in the upper electrode holder.
3. Fit a disk electrode onto the platinum mandrel and insert into the rotating disk assembly as the lower electrode.
4. Adjust the electrodes to give a 3 mm gap, centered about the optical axis of the spectrograph, and maintain the gap throughout the exposure.
5. Position a Teflon sample dish under the disk electrode and transfer the sample solution into it with a plastic pipette.
6. Excite the sample with the spark discharge, using the following parameters:

Capacitance	0.005 μ f
Inductance	310 μ h
Resistance in Series with Gap	Residual
Primary Voltage	205
Radio-frequency Current	5.5 amp
Discharge Breaks per Half Cycle	4

6. Expose the plate under the following exposure conditions:

Spectral Region	2250 - 3300 Angstroms
Slit Width	25 microns
Slit Height	4 mm
Preburn	30 seconds
Exposure	120 seconds

Photographic Plate Handling Procedure

1. With only the dark room safe light on, develop the plate for 2 minutes at 68°F.
2. Place the developed plate in the short stop bath for 20 seconds.
3. Place the plate in the fixing bath for 2 minutes.
4. Wash the plate for 2 minutes.
5. Rinse the plate with distilled water, remove the excess water with a cellulose sponge and dry the plate on a plate dryer.

Photographic Plate Reading Procedure

1. Using the Jarrell-Ash comparator-microphotometer, visually compare the densities of the analytical lines with those on a standard plate to determine the concentrations of elements sought in the sample. The palladium additive will serve as a reference.
2. For use of the added palladium as an internal standard, measure the transmittances of the analytical and internal standard lines and convert these data to log intensity ratios. Obtain the concentration of each element in micrograms per gram of sample (ppm) from an appropriate calibration curve.
3. The following lines are used in the identification and estimation of the elements.

<u>Element</u>	<u>Wave Length, Angstroms</u>			
Ga	2874.24	2943.64		
Hf	2898.26	2916.48	2940.77	3072.88
Mo	2671.83	2816.15		
Nb	2673.57	3094.18		
Ta	2675.9	2685.11		
Ti	2531.25	3088.02		
V	2690.24	2920.38	2924.64	3093.11
Zr	2567.64	2568.87	2571.39	
Pd (Internal Standard)	2593.27	3114.04		

Discussion

It is important that the sample be dissolved completely; otherwise, undissolved tungsten will separate along with the chloroform phase and be carried through to the residue.

The rotating disk electrode system was selected for its good reproducibility and efficiency of solution excitation. Spark excitation of solutions by this technique also produces low background interference from small amounts of tungsten which may inadvertently be carried into the organic phase.

In a routine procedure for the analysis of uranium solutions, a mixture of isoamyl alcohol and chloroform is used to dissolve the cupferrides; in this procedure for tungsten samples, however, chloroform is used alone as extractant for the cupferrides; this reduces the amount of tungsten extracted.

References

- (1) Rodden, C. J., Current Procedures for the Analysis of UO_3 , UF_4 , and UF_6 , United States Atomic Energy Commission, Technical Information Service, February, 1956 (TID-7003), pp. 110-114. UNCLASSIFIED
- (2) Jones, Ralph J., ed., Selected Measurement Methods for Plutonium and Uranium in the Nuclear Fuel Cycle, United States Atomic Energy Commission, Division of Technical Information, 1963 (TID-7029), pp. 383-385. UNCLASSIFIED
- (3) Sugawara, Ken F., "Spectrophotometric Determination of Trace Amounts of Zirconium, Titanium, and Molybdenum in Tungsten using an Ion Exchange Separation," Analytical Chemistry, 36, No. 7, 1373-1374 (1964).

APPENDIX D

SPECTROCHEMICAL DETERMINATION OF THE PLATINUM GROUP
ELEMENTS IN TUNGSTEN POWDER USING THE ZINC REDUCTION SEPARATION

Scope and Sensitivity

This method is applicable to the determination of certain metallic impurities in tungsten powder which can be separated by reduction with zinc. Since the method was developed particularly for relatively pure materials, modifications may be necessary if applied to samples containing more than 100 ppm of these impurities.

The elemental coverage and limits of detection (estimated visually) for the procedure are listed in table VI .

TABLE VI

SPECTROCHEMICAL SENSITIVITIES FOR THE PLATINUM
GROUP ELEMENTS IN TUNGSTEN POWDER SAMPLES

<u>Element</u>	<u>Limit of Detection (ppm)</u>	<u>Element</u>	<u>Limit of Detection (ppm)</u>
Au*	1	Pt	1
Ir	1	Rh	1
Pd	1	Ru	1

* If Au is to be determined, a separate sample must be processed and palladium added as the gathering agent.

Summary of the Method

The platinum group elements are separated from solution by reduction with zinc (1,2,3), using gold as a gathering agent. The precipitate is filtered and ignited; the residue is placed in a graphite electrode and excited with the direct current arc. Comparison of the resulting photographic plates to standard plates is made visually for determination of concentrations.

Precision

The estimated 95% confidence limits of a single measurement are +100% and -50% of the value, at concentrations near the limit of detection.

Apparatus and Reagents

Gold solution: Dissolve 2.5 g of gold in a solution of 3 ml of nitric acid, 18 ml of hydrochloric acid, and 9 ml of water. Evaporate the solution to a paste on a steam bath, add 10 ml of hydrochloric acid and evaporate again. Repeat this evaporation operation a total of three times; if metallic gold precipitates, add a few crystals of sodium chlorate to redissolve the gold. Finally, add 10 ml of hydrochloric acid to the paste and dilute the solution to 500 ml in a volumetric flask.

Palladium solution: Dissolve 2.5 g of palladium in 10 ml of hydrochloric acid and dilute to 500 ml.

Hydrogen peroxide, reagent grade.

Sodium hydroxide solution, 20%.

Sulfuric acid, 9M.

Hydrochloric acid, 2%.

Ammonium hydroxide, concentrated and 1%.

Tartaric acid, powdered, reagent grade.

Ice bath.

Metallic zinc, 20 mesh.

Filter paper, Whatman No. 42.

Clay crucible, 25 ml.

Muffle furnace.

Hot plate.

Spectrograph, Jarrell-Ash (Wadsworth).

Power source, direct current (motor generator set).

Comparator-microphotometer, Jarrell-Ash or equivalent.

Electrodes, graphite:

Lower: 3/16 inch undercut, Ultra Carbon type 4880 or equivalent.

Upper: 1/8 inch rod, 1-1/2 to 2 inches long, pointed with a pencil sharpener.

Graphite powder, National Carbon Company SP-2 or equivalent.

Photographic plate, Eastman Kodak Spectrum Analysis No. 1.

Developer, Eastman Kodak D-19.

Acid short stop, Eastman Kodak SB-1.

Photographic fixer, Eastman Kodak F-5.

Sample Preparation Procedure

1. Weigh 5 grams of the sample into a 400 ml beaker and add 25 ml of distilled water.
2. Add hydrogen peroxide in small amounts with a minimum of heating until the sample is dissolved.
3. Place the sample in an ice bath and cool.
4. Adjust to a pH of 10 by adding a 20% solution of NaOH while the sample remains in the ice bath. (Keeping the sample cool prevents volatilization of ruthenium.)
5. Place the sample on a hot plate and warm to expel the hydrogen peroxide. (The sample turns from yellow to colorless.)
6. Dilute the solution to 250 ml with distilled water.
7. Add 50 grams of tartaric acid and dissolve.
8. Adjust the pH to 0.5 with 1:1 H_2SO_4 .
9. Add 1.0 ml of the gold* solution, then 5 grams of zinc, to reduce the solution and form a precipitate of the platinum group metals.
10. Place the solution on a hot plate, heat to a temperature of 80° to $90^{\circ}C$. for three hours, and let stand overnight.
11. Dissolve the excess tungsten by neutralizing the solution with concentrated ammonium hydroxide.
12. Filter the solution through a Whatman No. 42 filter paper.
13. Wash the precipitate thoroughly with 5% ammonium hydroxide, followed by successive washes with distilled water and hot 2% hydrochloric acid. (Adequate washing is necessary to ensure that the zinc and tungsten are removed.)

* If Au is to be determined, a separate sample must be processed and 1 ml of palladium solution added as the gathering agent.

14. Transfer the paper to a clay crucible and ignite at 500°C.
15. Break up the residue with a spatula, transfer quantitatively to an electrode and add 5 mg of graphite.

Spectrograph Operation Procedure

1. Position the plate holder containing two plates on the spectrograph and make appropriate adjustments to operate as follows:

Arc Stand Position	50 cm from slit
Condensing Lens	37.5 cm from slit
Slit Height	3 mm
Slit Width	30 microns
Collimating Mirror Mask	20 mm x 135 mm
Automatic Feed (for plate)	On and set for 3 mm automatic rack down
Timer	On and set for 60 seconds
Rack Switch	In "Raise" position
Condensing Lens	100 mm cylindrical
Slit Lens	450 mm cylindrical
Filter	None
Wave Length Setting	5750 Angstroms at center of plate holder
Excitation	Current regulator set at 11 amperes dc
Step Filter	Medium step

2. Wipe off the electrode clamps; insert the electrodes and adjust the gap distance to 4 millimeters by adjusting the projected image of the gap on the target screen.
3. Turn on the dc arc, adjust the source to 11 amperes, and excite for 60 seconds.
4. Maintain the 4 millimeter gap distance throughout the exposure by adjusting the electrodes when necessary.

5. At the completion of the exposure, remove the electrodes and discard.
6. Repeat the exposure cycle for the next sample.

Photographic Plate Handling Procedure

1. With only the darkroom safe light on, develop the plates for 2 minutes at 68°F.
2. Place the developed plates in the short stop bath for 20 seconds.
3. Place the plates in the fixing bath for 2 minutes.
4. Wash the plates for 2 minutes.
5. Rinse the plates with distilled water, remove the excess water with a cellulose sponge and dry the plates on a plate dryer.

Photographic Plate Reading Procedure

1. Using the Jarrell-Ash comparator-microphotometer, visually compare the densities of the lines with those on a standard plate to determine the concentration of elements sought in the sample.
2. The following lines are suggested for use in the identification and estimation of the elements:

<u>Element</u>	<u>Wave Length, Angstroms</u>			
Au	2427.95	2675.95		
Ir	2543.97	2661.98	2664.8	3220.78
Pd	2447.91	2476.42	3404.6	3421.24
Pt	2659.45	2997.97	3042.6	3064.71
Rh	2555.36	3396.85	3434.89	3462.04
Ru	2678.76	2988.95	3428.31	3436.74

Discussion

It is important that the sample be dissolved completely; otherwise, undissolved tungsten will be carried through to the residue. The precipitate formed in the procedure must also be washed thoroughly to remove the tungsten.

References

- (1) Rodden, C. J., Current Procedures for the Analysis of UO₃, UF₄, and UF₆, United States Atomic Energy Commission, Technical Information Service, February, 1956 (TID-7003), pp. 115-117. UNCLASSIFIED

- (2) Kolthoff, I. M. and Elving, P. J., Treatise on Analytical Chemistry, Part II, Volume 8, Interscience Publishers, New York - London, 1963, p. 422.
- (3) Hillebrand, W. F. and Lundell, G. E. F., Applied Inorganic Analysis, John Wiley and Sons, Inc., New York, 1948, p. 274.

APPENDIX E

SPECTROCHEMICAL DETERMINATION OF THE RARE EARTH
ELEMENTS IN TUNGSTEN POWDER

Scope and Sensitivity

This method is applicable to the determination of rare earth elements in tungsten powder. Since the method was developed particularly for relatively pure materials, modification may be necessary if applied to samples containing more than 100 ppm of these impurities.

The elemental coverage and limits of detection (estimated visually) for the procedure are listed in table VII.

TABLE VII

SPECTROCHEMICAL SENSITIVITIES FOR THE RARE EARTH
ELEMENTS IN TUNGSTEN POWDER

<u>Element</u>	<u>Limit of Detection (ppm)</u>	<u>Element</u>	<u>Limit of Detection (ppm)</u>
Ce	1	Nd	0.5
Dy	0.5	Pr	0.5
Er	0.5	Sm	0.5
Eu	0.5	Tb	0.5
Gd	0.5	Th	0.5
Ho	0.5	Tm	0.5
La	0.5	Yb	0.5
Lu	0.5	Y	0.5*

* If Y is to be determined, a separate sample must be processed and lanthanum added as the gathering agent.

Summary of the Method

The sample is dissolved with hydrogen peroxide, and the rare earths are precipitated with ammonium hydroxide (1). After filtering, the precipitate is ignited and placed into a graphite electrode and excited with the direct current arc. Comparison of the resulting photographic plate to standard plates is made visually.

Precision

The estimated 95% confidence limits of a single measurement are +100% and -50% of the value, at concentrations near the limit of detection.

Apparatus and Reagents

Spectrograph, Jarrell-Ash (Wadsworth).

Power source, direct current (motor generator set).

Photographic plates, Eastman Kodak Spectrum Analysis No. 1.

Filter, plate glass with mount.

Comparator, Applied Research Laboratories or equivalent.

Graphite powder, National Carbon Company SP-2 or equivalent.

Electrodes, graphite:

Lower: 3/16 inch undercut Ultra Carbon type 4880 or equivalent.

Upper: rod, 1/8 inch diameter, pointed with a pencil sharpener.

Filtering funnels, glass.

Beakers, glass.

Muffle furnace.

Yttrium solution: Dissolve 0.1270 g of spectrographically pure Y_2O_3 in a minimum volume of nitric acid and dilute to 100 ml with water. This solution contains 1 mg Y/ml.

Lanthanum solution: Dissolve 0.1170 g of spectrographically pure La_2O_3 in a minimum volume of nitric acid and dilute to 100 ml with water. This solution contains 1 mg La/ml.

Hydrogen peroxide, 30%, reagent grade.

Ammonium hydroxide, concentrated, reagent grade.

Filter paper, Whatman No. 40.

Filter tablet, Whatman.

Developer, Eastman Kodak D-19.

Acid short stop, Eastman Kodak SB-1.

Photographic fixer, Eastman Kodak F-5.

Separation Procedure

1. Weigh 5 grams of tungsten powder into a 400 ml beaker. (Prepare duplicate portions of each sample since two spectrographic settings are required.)

2. Add 25 ml of water to the beaker and add hydrogen peroxide in small increments until the sample is dissolved. It may be necessary to heat the sample in order to complete dissolution.
3. Place the sample on a hot plate and boil for a few minutes.
4. Add 2 ml of the yttrium* solution (serves as gathering agent).
5. Cool the solution and carefully add ammonium hydroxide until it is alkaline.
6. Add 40 ml of concentrated ammonium hydroxide in excess.
7. Add one quarter of a filter tablet to the solution and boil for two minutes.
8. Remove the solution from the hot plate and allow 10 minutes for the solids to settle.
9. Filter the sample through a Whatman No. 40 filter paper.
10. Wash the residue 5 times with 5% ammonium hydroxide solution.
11. Transfer the filter paper to a clean 30 ml platinum crucible and ignite at 800°C. in a muffle furnace until the carbon is removed.
12. Transfer the residue to a 3/16 inch undercut electrode and add 5 mg of graphite powder.

Spectrograph Operation Procedure

1. Position the plate holder containing two plates on the spectrograph and make appropriate adjustments to operate as follows:

Arc Stand Position	50 cm from slit
Slit Height	3 mm
Slit Width	30 microns
Collimating Mirror Mask	20 mm x 135 mm
Automatic Feed (for plate)	On and set for 3 mm automatic rackdown
Timer	On and set for 120 seconds
Rack Switch	In "Raise" position
Condensing Lens	100 mm cylindrical

* If Y is to be determined, a separate sample must be processed and 2 ml of lanthanum solution added as the gathering agent.

Slit Lens	450 mm cylindrical
Filter	None
Wave Length Setting	5750 Angstroms at center of plate holder
Excitation	Current regulator set at 11 amperes dc
Step Filter	Medium step

2. Wipe off the electrode clamps; insert the electrodes and adjust the gap distance to 4 millimeters by adjusting the projected image of the gap on the target screen.
3. Turn on the dc arc, adjust the source to 11 amperes, and excite for 120 seconds.
4. Maintain the 4-millimeter gap distance through the exposure by adjusting the electrodes when necessary.
5. At the completion of the exposure, remove the electrode and discard.
6. Repeat the exposure cycle for the duplicate sample, using the same conditions as above, with the following changes:

Condensing Lens	None
Filter	Glass
Wave Length Setting	7500 Angstroms at center of plate holder

Photographic Plate Handling Procedure

1. With only the dark room safe light on, develop the plates for 2 minutes at 68°F.
2. Place the developed plates in the short stop bath for 20 seconds.
3. Place the plates in the fixing bath for 2 minutes.
4. Wash the plates for 2 minutes.
5. Rinse the plates with distilled water, remove the excess water with a cellulose sponge and dry the plates on a plate dryer.

Photographic Plate Reading Procedure

1. Using the ARL comparator (or equivalent) visually compare the density of the lines with those on a standard plate to determine the concentration of elements sought in the sample.
2. The following lines are suggested for use in the identification and estimation of the rare earth elements:

<u>Element</u>	<u>Wave Length, Angstroms</u>				
Ce	4186.6	4296.6			
Dy	3169.97	3385.027	3393.6	3407.8	
Er	3230.59	3264.78			
Eu	2668.3	2727.78	2906.67	2925.03	
Gd	3100.5	3350.482	3358.6	3422.46	
Ho	3398.98	3456.0			
La	3245.12	3337.5	3380.9		
Lu	2615.4	2894.8	2900.3	2911.39	3077.6
Nd	4303.5				
Pr	4222.98	4225.3			
Sm	3273.48	4256.4	4262.68	4279.68	4280.78
Tb	3219.95	3293.1	3324.4		
Th	2851.26	2899.72	3088.47	3108.3	3119.5
	3180.2	3235.85	3238.12	3262.67	3291.74
	3292.52				
Tm	3131.26	3133.88	3151.035	3157.34	3362.61
Yb	2891.39	3289.37			
Y	3200.3	3203.3	3216.7	3242.3	3327.9

Discussion

Duplicate 5-gram portions of each sample must be processed in this procedure because two wavelength settings must be employed on the spectrograph to record the spectra of all the rare earth elements.

The amount of tungsten carried through the procedure must be kept to an absolute minimum because of the interfering spectrum it produces. The tungsten must be completely dissolved in the dissolution operation; otherwise it will be filtered out and subsequently ignited with the rare earths. Complete washing of the tungsten from the residue in step 10 is also very important.

References

- (1) Kolthoff, I. M. and Elving, P. J., Treatise on Analytical Chemistry, Part II, Volume 8, Interscience Publishers, New York - London, 1963, pp. 36-40.