MAB-217-M

COOPERATIVE ANALYSIS PROGRAM
ON
REFRACTORY METAL ALLOYS

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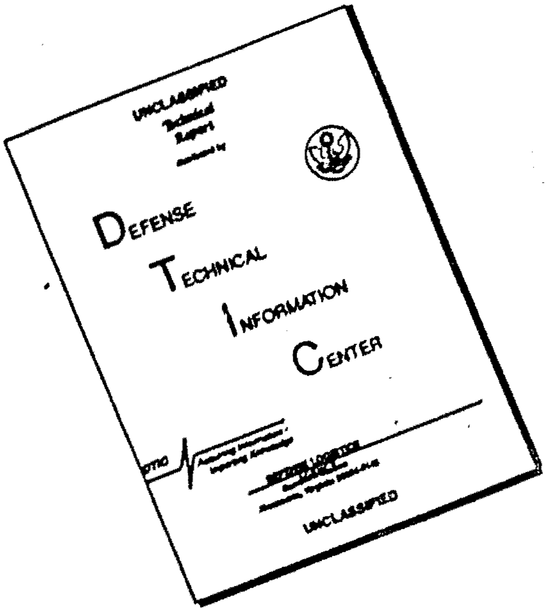

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Report of the

SUBPANEL ON ANALYSIS METHODS

REFRACTORY METALS SHEET ROLLING PANEL

COOPERATIVE ANALYSIS PROGRAM

ON

REFRACTORY METAL ALLOYS

Prepared By The

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Division of Engineering and Industrial Research
National Research Council

as a service of

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to the

Office of Defense Research and Engineering
Department of Defense

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ABSTRACT

As a part of the Refractory Metals Sheet Rolling Program, reference materials (unalloyed W, T-111 Ta, FS-85 Cb, and TZM Mo) were prepared and analyzed by 25 cooperating laboratories. No serious problems were encountered in determining alloying elements. Hydrogen and carbon determinations could be made satisfactorily at the levels encountered, but agreement on oxygen and nitrogen was not satisfactory below the 10 ppm level. Recommendations for research to solve remaining problems are offered.

COOPERATIVE ANALYSIS PROGRAM

ON

REFRACTORY METAL ALLOYS

I. INTRODUCTION

The existence of specific problems in chemical analysis is generally not recognized until cooperative analytical studies have been carried out on materials of interest. While there has been continuing activity in analysis of the unalloyed refractory metals, as exemplified by the work carried out in ASTM Division I and R of Committee E-3, and the Analytical Subpanel of the Structures and Materials Panel of AGARD* (NATO), at the beginning of this program no such activity existed for refractory metal alloys. Therefore, it was considered of highest priority in the work of the Analysis Methods Subpanel to institute a cooperative analysis program on representative alloys of importance, in order to check the levels of agreement being obtained in the determination of alloying constituents and impurities with existing techniques, identify problem areas, and permit an exchange of information among laboratories engaged in analysis of refractory alloys.

II. PREPARATION AND SCREENING OF REFERENCE MATERIALS

In order to conduct such cooperative studies, standard or reference samples of the materials under consideration must be prepared and distributed to the participants. Since the highest uniformity is essential in the reference materials, it was necessary to have these specially produced for the program. Under sponsorship of the Bureau of Naval Weapons, the task of procuring and checking the uniformity of the reference materials was placed in the hands of the Albany Metallurgical Center of the United States Bureau of Mines. This effort, which is reported in a series of

*Advisory Group for Aeronautical Research Development - to date the work in ASTM has been concentrated on Cb, Mo, and W, while the AGARD work is largely directed toward Ta. The AGARD program in the past has also included Cb, Mo, and W.

Quarterly Progress Reports and a Final Material Screening Report* from the organization, resulted in the preparation of four alloys of the following compositions:

SELECTED RESULTS FROM 25 COOPERATING LABORATORIES

DATA IN ROUNDS 1 and 2

	Unalloyed W	T-111	FS-85	TZM
W		7.88%	10.11%	---
Ta		----	27.67%	---
Zr		----	0.92%	0.089%
Ti		----	----	0.50%
Hf		1.75%	----	---
C	9.1 ppm	17 ppm	10 ppm	230 ppm
O	7.3 ppm	14 ppm	68 ppm	7.1 ppm
N	6.3 ppm	18 ppm	43 ppm	16 ppm
H	0.47 ppm	24 ppm	1.3 ppm	0.49 ppm

These materials were obtained as finished 1/4" diameter rod (approximately 25 pounds) and sufficient billet to permit machining approximately 25 pounds of sample chips. The unalloyed W was obtained in rod form only and was produced by powder metallurgy methods. Suppliers of the rod and billet were the following:

Unalloyed W	General Electric Company, Cleveland
T-111	Wah Chang Corp., Albany
FS-85	Fansteel Metallurgical Corp.
TZM	Climax Molybdenum Company

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*Quarterly progress reports dated March 1963, June 1963, September 1963, December 1963, and March 1964. Final Material Screening Report USBM-U-1100, February 10, 1964, R.A. Beall, D.M. Mortimore, and E.D. Calvert. BuWeps Order #TPR1963-1964-8042 (WEPS).

The T-111 and FS-85 alloys were produced by electron beam melting followed by double consumable electrode arc melting, while the TZM was produced by consumable arc melting. After extrusion or forging, the ingots were worked down to 1/4" rod. A portion of the ingots was set aside for chip machining. The 1/4" rods were supplied in lengths of 8 to 10 feet with each length given a rod identification number to catalogue position. The FS-85 and W rods were, unfortunately, delivered to the Bureau of Mines with no information concerning orientation of the individual rods to each other. The TZM and T-111 rods, on the other hand, were well documented. Each rod was sampled approximately every two feet for the determination of H, N, and O. Carbon and the major alloying elements were determined from the machined chips screened to +16 mesh and then thoroughly mixed. Ten random samples were taken. Further screening of the reference materials was performed by the Army Materials Research Agency (Watertown), du Pont, Westinghouse, and Battelle. A summary of the Bureau of Mines results is given in Table I. While the indicated homogeneity left something to be desired, it was felt that the materials could be used for reference purposes with judicious selection of rods. There was a strong indication that the materials might be more homogeneous than the Bureau of Mines' results suggested. Therefore, the chips and selected rods chosen as follows were approved for distribution to cooperating laboratories: FS-85: NA-1, NA-3, NA-4, NA-6, NA-10; T-111: T-2, T-3, T-4; TZM: M-2, M-12, M-21; W: WPM-1, WPM,2, WPM-3, WPM-4, WPM-5.

TABLE I

Summary of Bureau of Mines Screening Analysis of Reference Alloys

UNALLOYED TUNGSTEN

	C	O	N	H
Average, ppm	26	14	5	2.1
Standard Deviation, ppm	10.2	2.2	4.1	0.6
Coefficient of Variation,%	39.2	15.7	82.0	28.6

T-111

	C	O	N	H	W	Hf
Average	49 ppm	20 ppm	25 ppm	19 ppm	7.59%	1.87%
Std. Dev.	13.6 "	2.4 "	5.9"	4.7 "	0.52%	0.11%
Coef.of Var. %	27.1	12.0	23.6	24.5	6.8	5.9

FS-85

	C	O	N	H	W	Zr	Ta
Average	32 ppm	59 ppm	33 ppm	0.7 ppm	8.80%	0.86%	27.4%
Std. Dev.	10.8 "	10.2 "	7.9 "	0.27 "	0.45%	0.084%	0.42%
Coef.of Var.%	33.7	17.3	24.0	38.5	5.1	9.7	1.5

T2M

	C	O	N	H	Ti	Zr
Average	241 ppm	17 ppm	9 ppm	0.6 ppm	0.43%	0.10%
Std. Dev.	19.6 "	3.8 "	3.5 "	0.28 "	0.03%	0.005%
Coef. of Var.%	8.1	22.4	39.0	46.7	7.0	5.0

III. COOPERATIVE ANALYSIS PROGRAM (ROUND ROBINS)

Participants in the round robins included DOD contractors involved in the refractory metals sheet rolling program, government agencies laboratories, and other interested organizations with experience in the analysis of refractory metals. A list of the 25 organizations taking part voluntarily in this activity is given in Table II. The goals for interlaboratory agreement at the end of the program, particularly for the gaseous elements were set as follows:

Level, ppm	Standard Deviation, ppm	Coefficient of Variation, %
10,000	250	2.5
1,000	50	5
100	10	10
10	2	20
1	0.4	40

It is seen that as the level drops by one order of magnitude, the standard deviation drops by a factor of 5, and the coefficient of variation doubles. The deviation necessarily includes any inhomogeneity of the reference material as well as the factors of within-laboratory reproducibility, and interlaboratory agreement.

TABLE II

Participants in MAB-RMSRP Cooperative Analysis Program

Participant	Designation
Aerojet General Corporation	A
Army Materials Research Agency	B
Battelle Memorial Institute	C
Boeing Aircraft Company	D
Climax Molybdenum Company	E
Du Pont	F
Fansteel Metallurgical Corporation	G
General Atomic Div. of General Dynamics Corp.	H
General Electric, Cleveland	I
Iowa State University	J
Ledoux and Company	K
Lewis Research Center, NASA	L
Metals and Controls, Inc.	M
National Research Corporation	N
Oak Ridge National Laboratories	O
Oregon Metallurgical Corporation	P
Pratt & Whitney - Canal	Q
Sylvania Electric Products Inc.	R
Universal Cyclops Steel Corporation	S
U.S. Bureau of Mines, Albany	T
U.S. Bureau of Mines, Boulder	U
U.S. Naval Air Engineering	V
Wah Chang Corporation	W
Westinghouse Electric Corporation	X
Wright-Patterson Air Force Base	Y

ROUND ROBIN #1*

The first round robin was intended to be highly exploratory in character. Therefore, the ground rules were held to a bare minimum and cooperators were given a wide latitude in the selection of procedural details. It was assumed that each cooperator would employ the methods that he normally would use in analysis of the compositions under test, and that maximum sample sizes would be: oxygen, 2 gms; hydrogen, 1 gm; nitrogen, 2 gms; carbon, 1 gm; alloying constituents, 1 gm. Participants were sent 15 gms of TZM and FS-85 chips; 12 gms of T-111 chips; 50 gms of TZM and W rod; and 20 gms of T-111 and FS-85 rod. The following instructions were also issued to participants:

A. Ground Rules - Round Robin #1

1. Analyses to be performed are: oxygen, hydrogen, nitrogen, and carbon in FS-85, TZM, and unalloyed tungsten; oxygen, hydrogen, and nitrogen in T-111; tantalum, zirconium and tungsten in FS-85; tungsten and hafnium in T-111; titanium and zirconium in TZM.

2. All analyses will be performed three times, once each on three different days.

3. All analyses for oxygen, hydrogen, and nitrogen will be made on solid, undivided samples. There will be no exceptions from this ground rule.

4. All solid specimens will be prepared by filing followed by rinsing in a residue-less solvent.

5. All nitrogen determinations will be made by the Kjeldahl or micro Kjeldahl procedure.

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*Results of round robins #1, #2, and #3 are presented in detail in DMIC Report No. 220 entitled, "Comparison of Chemical Analysis of Refractory Alloys," by D. L. Chase.

6. Carbon and alloying metals will be determined on subdivided samples.

7. The cooperator will subdivide the tungsten sample for carbon determination.

B. Information Reporting - Round Robin #1

Reports of analytical results should be forwarded to Mr. D. L. Chase of the Defense Metals Information Center at Battelle Memorial Institute, 505 King Street, Columbus, Ohio. All reports should contain the following information:

1. Tabulations of all individual results. No result should be omitted except for a sound technical reason.

2. Indication of deviation from any of the simple ground rules.

3. Indication of whether or not the work was performed internally. If performed externally, indicate name and address of organization performing the analyses.

4. A brief summary of the methods employed as follows:

(a) Oxygen and Hydrogen
Type of equipment used
Sample size
Temperature and extraction time
Bath or flux, if any (indicate composition)
Direct or indirect measurement of CO_2 or H_2
If empirical, indicate method of calibration

(b) Nitrogen
Indicate Kjeldahl or micro Kjeldahl
Sample size
Method of NH_3 estimation

(c) Carbon

Type of equipment used

Sample size

Fluxes or modifiers used (state composition)

Method of CO_2 measurement

If empirical, indicate method of calibration

For tungsten, indicate method and degree of subdivision

(d) Alloying Metals

Indicate method employed

Sample size

If empirical, indicate method of calibration

C. Results and Discussion - Round Robin #1

Results were compiled and statistically analyzed by D. L. Chase of Battelle Memorial Institute* and were discussed at a meeting of the subpanel, Government liaison representatives, and cooperating members on August 6, 1964. A summary of the data from round robin #1 is given in Tables III-IX.

The large scatter in results shown in the tables of data are to be expected in the initial round and point up the fact that many variables in methods must be brought under control before reasonable agreement between laboratories can be achieved. This is especially true in the analysis of such materials as the four alloys used in this program.

By eliminating some of the extreme values (but retaining at least 75% of the data), the picture is improved somewhat. The coefficients of variation for selected hydrogen results are all less than twice the goal. The selected values for C, N, and O yield coefficients of variation which are clustered near twice the goal, as shown in Figure 1.

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*See DMIC Report #220.

Perhaps the most important part of any cooperative program such as this is the discussion of the work by the participants. Ideas can be exchanged, instruments and techniques can be discussed and many problems can be worked out. At the August 6, 1964 meeting, the results of round robin #1 were thoroughly examined and the following conclusions were reached:

1. There seemed to be no particular difficulty in determining alloying elements and work on these should be terminated.

2. The determination of C in the TZM alloy appeared to be satisfactory and no more work was required.

3. The scatter in results of O, H, N and C (excepting C in TZM) indicated that some variables were not under control.

4. A second round robin involving only the elements O, H, N and C should be carried out with more rigid ground rules.

TABLE III

Round Robin #1, Summary of Results for Alloying Elements in T-111

	All Results - %		Selected Data - %	
	Hf	W	Hf	W
Average	1.74	7.87	1.75	7.88
Average Deviation	0.08	0.38	0.06	0.16
Standard Deviation	0.12	0.62	0.09	0.21
Coefficient of Variation	6.9%	7.9%	5.1%	2.7%
Range	1.53-1.85%	6.10-8.75%	1.55-1.83%	7.52-8.28%
Number of Values	13	14	11	11

Results Classified by Method

	X-Ray - %		Emission Spec.%		Chemical-%	
	Hf	W	Hf	W	Hf	W
Average	1.73	7.72	1.80	8.17	1.70	7.88
Average Deviation	0.11	0.55	0.02	0.37	0.08	0.18
Standard Deviation	0.13	0.87	0.03	0.53	0.11	0.25
Coefficient of Variation	7.5%	11.3%	1.7%	6.5%	6.5%	3.2%
Number of Values	6	6	3	3	4	5

Methods for Alloying Elements*
in T-111

Companies F, G, P, R, W, and X used X-ray;

Companies D, N and Q used emission spectroscopy for both Hf and W.

Companies B, K and T used ion exchange for both elements.

Company C used ion exchange for W and fluorohafnate separation, weighed as phosphate, for Hf.

*For Further Details see DMIC Report #220 by D.L. Chase

TABLE IV

Round Robin #1, Summary of Results for Alloying Elements in FS-85

	All Results-%			Selected Data-%		
	Ta	W	Zr	Ta	W	Zr
Avg.	28.05	10.50	0.94	27.67	10.11	0.92
Avg. Dev.	1.05	0.62	0.15	0.51	0.17	0.065
Std. Dev.	1.41	0.83	0.24	0.67	0.22	0.092
Coef.of Var.	5.0	7.9	25.5	2.4	2.2	10.0
Range	26.35-31.3	9.75-12.6	0.46-1.54	26.8-28.8	9.75-10.53	0.76-1.05
No. of Values	13	14	13	10	11	10

Results Classified by Method

	X-ray-%			Emission Spec.-%			Chemical - %		
	Ta	W	Zr	Ta	W	Zr	Ta	W	Zr
Avg.	28.73	10.92	0.98	27.47	10.77	1.13	27.72	10.01	0.80
Avg. Dev.	1.65	0.95	0.11	0.76	0.53	0.28	0.51	0.14	0.15
Std. Dev.	1.95	1.14	0.135	1.14	0.72	0.37	0.78	0.19	0.20
Coef. of Var.	6.8	10.4	13.8	4.1	6.7	32.8	3.1	1.9	25.0
No. of Values	5	5	5	3	3	3	5	6	5

Methods for Alloying Elements
in FS-85

Companies F, G, P, R, and X used X-ray; D, Q, and S used emission spectroscopy for all alloying elements.

Companies B, K, T used ion exchange for all elements; company C for Ta and W; and company W for Ta and Zr.

Company C used fluo-zirconate separation, phosphate precipitation for Zr, while company W used dithiol extraction-photometric for W.

TABLE V

Round Robin #1, Summary of Results for Alloying Elements in TZM

	All Results - %		Selected Data-%	
	Ti	Zr	Ti	Zr
Avg.	0.51	0.090	0.50	0.089
Avg. Dev.	0.023	0.0058	0.010	0.0038
Std. Dev.	0.037	0.0076	0.013	0.0055
Coef. of Var.	7.2	8.5	2.6	6.2
Range	0.44-0.60	0.078-0.103	0.47-0.52	0.081-0.099
Number of Values	13	13	10	10

Results Classified by Method

	X-Ray - %		Emis.Spec.-%		Chemical-%	
	Ti	Zr	Ti	Zr	Ti	Zr
Avg.	0.54	0.093	0.50	0.090	0.49	0.088
Avg. Dev.	0.037	0.005	0.010	0.006	0.023	0.006
Std. Dev.	0.050	0.006	0.012	0.009	0.032	0.0085
Coef. of Var.	9.3	6.3	2.4	10.	6.5	9.7
No. of Values	3	4	3	3	7	6

Methods for Alloying Elements
in TZM

Companies F, G, P used X-ray for both elements and X for Zr.

Companies D, E, R used emission spectroscopy for both elements.

Companies B, T, W used ion exchange for both.

Companies C, K, S used NH_4OH separation, and company X used spectrophotometric for Ti.

TABLE VI

Round Robin #1, Summary of Results for Carbon

All Results (PPM)

	FS-85	TZM	T-111	Tungsten
Average	18	228	19	22
Average Deviation	13	21	6.8	16
Standard Deviation	22.5	30.6	8.0	25.8
Coef. of Variation	125%	13.4%	42.0%	117%
Range	1-99	130-281	9-33	1-109
Number of Values	17	21	12	17

Selected Data (PPM)

	FS-85	TZM	T-111	Tungsten
Average	12	230	17	13
Average Deviation	2.9	12	4.8	5.1
Standard Deviation	3.7	16	5.9	6.3
Coef. of Variation	30.8%	6.9%	34.7%	48.5%
Range	8-19	206-260	10-25	4-25
Number of Values	13	17	9	13

Methods used for Carbon

Companies A-I, L, M, O-R, T and W used Leco Induction;
Companies K, N, S, and X used resistance furnaces.
All companies used Leco conductometric readout.

TABLE VII

Round Robin #1, Summary of Results for Nitrogen (Kjeldahl Only)

All Results (PPM)

	FS-85	TZM	T-111	Tungsten
Average	48	14	31	13
Average Deviation	22	4.7	22	8.8
Standard Deviation	38	5.9	41	16
Coef. of Variation	79.2%	42.1%	132%	123%
Range	15-173	3-53	2-162	3-62
Number of Values	15	13	13	12

Selected Data (PPM)

	FS-85	TZM	T-111	Tungsten
Average	41	12	20	8
Average Deviation	8	2.6	8.3	2.8
Standard Deviation	10	3.5	99.9	3.2
Coef. of Variation	24.4%	29.2%	49.5%	40.0%
Range	26-60	8-19	8-36	4-13
Number of Values	11	10	10	9

Results Classified by Method (PPM)

	Photometric				Titrimetric			
	FS-85	TZM	T-111	W	FS-85	TZM	T-111	W
Avg.	50	10	19	8	47	19	46	19
Avg. Dev.	28	4	10	3	14	12	39	17
Std. Dev.	48	5	11	3.5	19	17	59	24
Coef.of Var.	96.0%	50.0%	58.0%	43.8%	40.5%	89.5%	128%	126%
No.of Values	9	7	7	7	6	6	6	5

Methods used for Nitrogen

All companies reporting used micro Kjeldahl except S which used macro-K. Measurement was by both titration and Nessler.

TABLE VIII

Round Robin #1, Summary of Results for Oxygen

All Results (PPM)

	FS-85	TZM	T-111	Tungsten
Average	53	13.5	25.1	9.4
Average Deviation	14.5	6.7	14.2	4.4
Standard Deviation	21.2	9.3	32.2	5.4
Coef.of Variation	40.0%	68.9%	128%	57.5%
Range	15-117	2.8-45.0	7.6-162.0	2.1-18.0
Number of Values	22	20	21	20

Selected Data (PPM)

	FS-85	TZM	T-111	Tungsten
Average	52	12.0	18.5	9.1
Average Deviation	9.2	4.4	4.9	3.5
Standard Deviation	12.2	4.9	6.2	4.5
Coef. of Variation	23.5%	40.8%	33.5%	49.5%
Range	23-69	6.1-20.0	10-29	4-17
Number of Values	18	16	17	16

Results Classified by Method (PPM)

	Vacuum Fusion				Inert Gas Fusion			
	FS-85	TZM	T-111	W	FS-85	TZM	T-111	W
Avg.	51	11.4	27.5	7.9	57	19	20	12.8
Avg. Dev.	12	5.3	18.1	4.0	19	6.0	5.0	4.0
Std. Dev.	17	6.2	38.9	5.1	28	14	6.9	4.7
Coef.of Var.	33.4%	54.4%	141.0%	64.5%	49.1%	73.8%	34.5%	36.1%
No.of Values	14	14	14	14	8	6	7	6

Methods used for Oxygen

A great variety of equipment, extraction temperatures and times, fluxes, measurement and calibration methods were reported.

TABLE IX

Round Robin #1, Summary of Results for Hydrogen

All Results (PPM)

	FS-85	TZM	T-111	Tungsten
Average	2.0	1.0	26	0.86
Average Deviation	1.08	0.72	5.6	0.62
Standard Deviation	1.53	0.89	10.9	0.88
Coef. of Variation	76.5%	89.0%	42.0%	102.%
Range	0.5-6.6	0.1-3.5	2.-64	0.1-3.1
Number of Values	21	21	22	19

Selected Data (PPM)

	FS-85	TZM	T-111	Tungsten
Average	1.8	0.86	27	0.69
Average Deviation	0.75	0.55	2.5	0.39
Standard Deviation	0.90	0.65	3.2	0.44
Coef.of Variation	50.0%	75.5%	10.9%	63.8%
Range	0.5-3.6	0.2-2.0	19-30	0.2-1.4
Number of Values	17	17	18	15

Results Classified by Method (PPM)

	Vacuum Fusion				Hot Extraction			
	FS-85	TZM	T-111	W	FS-85	TZM	T-111	W
Avg.	2.1	0.97	26.1	0.77	1.8	1.0	25.4	1.1
Avg. Dev.	1.1	0.57	7.1	0.55	0.9	1.0	2.3	0.7
Std. Dev.	1.7	0.68	13.0	0.80	1.1	1.3	3.2	0.9
Coef.of Var.	81.0%	70.0%	49.8%	104%	61.0%	130%	12.6%	81.8%
No.of Values	14	14	15	13	7	7	7	6

Methods used for Hydrogen

See remarks for oxygen.

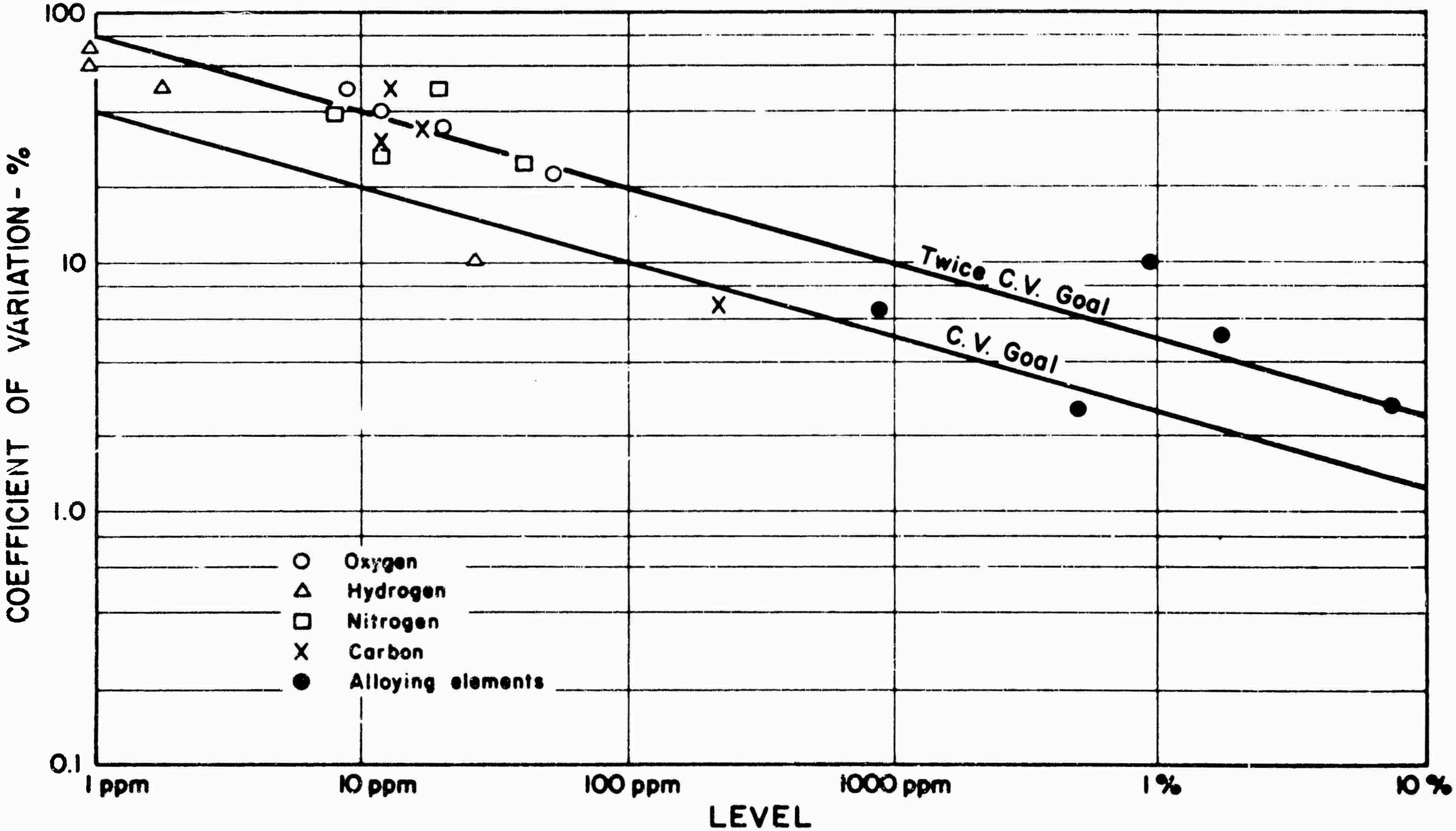

FIGURE 1. ROUND ROBIN NUMBER 1 SELECTED RESULTS
(75% retention of data)

ROUND ROBIN #2

Following a lengthy discussion at the above meeting, a set of ground rules to govern round robin #2 were worked out and are given below:

A. Ground Rules - Round Robin #2

1. Analyses to be performed are:

FS-85	Oxygen, hydrogen, nitrogen and carbon.
TZM	O, H, and N
T-111	O, H, N, and C
Unalloyed Tungsten	O, H, N, and C

2. All analyses will be performed three times, once each on three different days.

3. All analyses for O, H, and N will be made on solid, undivided samples. There will be no exceptions from this ground rule.

4. All solid samples will be prepared by filing followed by rinsing in a residue-less solvent.

5. All nitrogen determinations will be made by the Kjeldahl procedure.

6. Carbon will be determined on subdivided samples.

7. Specific solid samples will be provided for O, H, and N determinations.

8. A subdivided sample of tungsten will be supplied for the carbon determination.

Oxygen (Vacuum Fusion)

	FS-85	TZM	T-111	Tungsten
Sample Size	1 g	2 g	2 g	2 g
Bath or Flux	Pt	Pt-20Sn	Pt	Pt-20Sn
Final Ratio (Min.)	10:1 for all samples			
Temperature	1900-2000^{o}C for all samples			
Extraction Time	15-30 mins. for all samples			
Blank	2 micrograms or less per extraction period			
Measurement	Direct if possible			

Oxygen (Inert Gas Fusion)

Sample Size	2 g
Bath or Flux	Pt
Final Ratio (Min.)	5:1
Temperature	2200-2400°C
Time of Extraction	7 mins. - no cycling
Conductivity Solution	Either $Ba(OH)_2$ or NaOH
Calibration	Phthalate

Hydrogen (Hot Extraction)

	FS-85	TZM	T-111	Tungsten
Sample Size	2 g	2 g	1 g	2 g
Temperature	1300-1400°C for all samples			
Extraction Time	5 minutes for all samples			
Blank	Less than 0.2 microgram			
Measurement	Direct. Separate hydrogen by means of a palladium valve or oxidize H_2 to H_2O and absorb.			

Nitrogen (Kjeldahl)

	FS-85	TZM	T-111	Tungsten
Sample Size	1 g	1 g	1 g	2 g
Method of Solution	Dissolve 1 g. sample in 20 ml. of 1:1-48% HF and up to 15 ml. of 30% H_2O_2. The H_2O_2 is added 5 ml. at a time at 45-60 minute intervals. Dissolution is carried out in a polyethylene or platinum container (covered) immersed in a water bath at approximately 50°C.			Dissolve 2 g.sample in 40 ml. of 1:1 30% H_2O_2 at approximately 50°C.
Determination	Nessler-photometric			
Calibration	NH_4Cl carried through procedure			
Blank	Less than 2 micrograms if possible			

Carbon (Conductometric-Induction Heating)

Sample Size	2-3 g for all samples
Flux	0.5-1 g Fe and 1 g Sn or 1 g CuO and 1 g Sn
Calibration	Phthalate
Time	5 minute burn--5 minute sweep
Conductivity Solution	0.75 g $Ba(OH)_2$ per liter or the equivalent in NaOH

Carbon (resistance Furnace)

Temperature	1100-1400°C
Flux	At discretion of operators

Calibration, time and conductivity solution the same as for induction heating.

In addition, the size of the blank obtained while determining carbon, nitrogen and oxygen was requested.

B. Results and Discussion - Round Robin #2

Results are presented in the following Tables X to XIII, and in Fig. 2.

TABLE X

ROUND ROBINS #1 and 2, SUMMARY OF RESULTS FOR CARBON

	FS-85		TZM	T-111		Tungsten	
	No.1	No.2	No. 1	No. 1	No. 2	No.1	No. 2
All Results (ppm)							
Average	18	13	228	19	18	22	9.3
Average Deviation	13	5.68	21	6.8	3.89	16	2.89
Standard Deviation	22.5	8.23	30.6	8.0	5.26	25.8	4.70
Coefficient of Variation	125%	63.3%	13.4%	42%	29.2%	117%	50.5%
Range	1-99	3-37	130-281	9-33	12-32	1-109	5-26
Number of Values	19	19	21	12	19	17	19
Selected Data (ppm)							
Average	12	10	230	17	17	13	9.1
Average Deviation	2.9	2.34	12	4.8	2.20	5.1	1.67
Standard Deviation	3.7	2.74	16	5.9	2.82	6.3	2.12
Coefficient of Variation	30.8%	27.4%	6.9%	34.7%	16.6%	48.5%	23.4%
Range	8-19	5-14	206-260	10-25	13-23	4-25	5-12
Number of Values	13	15	17	9	15	13	15

TABLE XI

ROUND ROBINS #1 and 2, SUMMARY OF RESULTS FOR NITROGEN

	All Results by Kjeldahl (ppm)							
	FS-85		TZM		T-111		Tungsten	
	No.1	No.2	No.1	No.2	No.1	No.2	No.1	No.2
Avg.	48	45	14	16	31	20	13	9.5
Avg. Dev.	22	7.92	4.7	4.88	22	7.83	8.8	6.27
Std. Dev.	38	9.84	5.9	5.80	41	9.00	16	9.03
Coef. of Var.	79.2%	21.9%	42.1%	36.3%	132%	45.0%	123%	95.1%
Range	15-173	30-63	3-53	7-20	2-162	11-38	3-62	0.6-28
Number of Values	15	13	13	8	13	12	12	7

	Selected Data (ppm)							
Avg.	41	43	12	16	20	18	8	6.3
Avg. Dev.	8	4.80	2.6	3.67	8.3	5.56	2.8	3.17
Std. Dev.	10	5.84	3.5	4.25	9.9	6.25	3.2	4.09
Coef. of Var.	24.4%	13.6%	29.2%	26.6%	49.5%	34.7%	40%	65.0%
Range	26-60	35-51	8-19	11-21	8-36	11-26	4-13	0.6-12
Number of Values	11	10	10	6	10	9	9	6

TABLE XII

ROUND ROBINS #1 and 2, SUMMARY OF RESULTS FOR OXYGEN

	FS-85		TZM		T-111		Tungsten	
	No.1	No.2	No.1	No.2	No.1	No.2	No. 1	No. 2
All Results (ppm)								
Avg.	53	68	13.5	9.2	25.1	14.5	9.4	7.4
Avg. Dev.	14.5	13.5	6.7	4.42	14.2	4.21	4.4	3.52
Std. Dev.	21.2	17.1	9.3	6.15	32.2	4.91	5.4	4.02
Coef. of Var.	40%	25.2%	68.9%	66.9%	128%	33.9%	57.5%	54.4%
Range	15-117	42-103	2.8-45	3.6-27	7.6-162	7.2-24	2.1-18	2.4-137
Number of Values	22	18	20	18	21	18	20	18
Selected Data (ppm)								
Avg.	52	68	12	7.1	18.5	14	9.1	7.3
Avg. Dev.	9.2	9.36	4.4	1.97	4.9	3.28	3.5	2.96
Std. Dev.	12.2	11.5	4.9	2.44	6.2	3.85	4.5	3.42
Coef. of Var.	23.5%	16.9%	40.8%	34.4%	33.5%	26.9%	49.5%	46.9%
Range	23-69	50-87	6.1-20	3.6-12	10-29	8.6-19	4-17	2.5-11.3
Number of Values	18	14	16	14	17	14	16	14
Results by Activation Analysis (H)		73		4.6		7.2		6.0
Results by Activation Analysis (J)		61		7.9		11.		5.5

TABLE XIII

ROUND ROBINS #1 and 2, SUMMARY OF RESULTS FOR HYDROGEN

	All Results (ppm)							
	FS-85		TZM		T-111		Tungsten	
	No.1	No.2	No.1	No.2	No.1	No.2	No.1	No.2
Avg.	2.0	1.5	1.0	0.75	26	23	0.86	0.59
Avg. Dev.	1.08	0.63	0.72	0.54	5.6	6.42	0.62	0.42
Std. Dev.	1.53	0.82	0.89	0.75	10.9	8.10	0.88	0.60
Coef. of Var.	76.5%	54.6%	89.0%	100%	42.0%	35.2%	102.%	102%
Range	0.5-6.6	0.6-3.8	0.1-3.5	0.03-2.8	2.0-64	3-33	0.1-3.1	0.03-2.5
Number of Values	12	19	21	16	22	19	19	17
	Selected Data (ppm)							
Avg.	1.8	1.3	0.86	0.49	27	24	0.69	0.47
Avg. Dev.	0.75	0.39	0.55	0.22	2.5	4.60	0.39	0.24
Std. Dev.	0.90	0.51	0.65	0.28	3.2	5.81	0.44	0.33
Coef. of Var.	50.0%	39.2%	75.5%	57.2%	10.9%	24.2%	63.8%	63.9%
Range	0.5-3.6	0.6-2.0	0.2-2.0	0.13-1.1	19-30	11-31	0.2-1.4	0.14-1.0
Number of Values	17	15	17	12	18	15	15	13

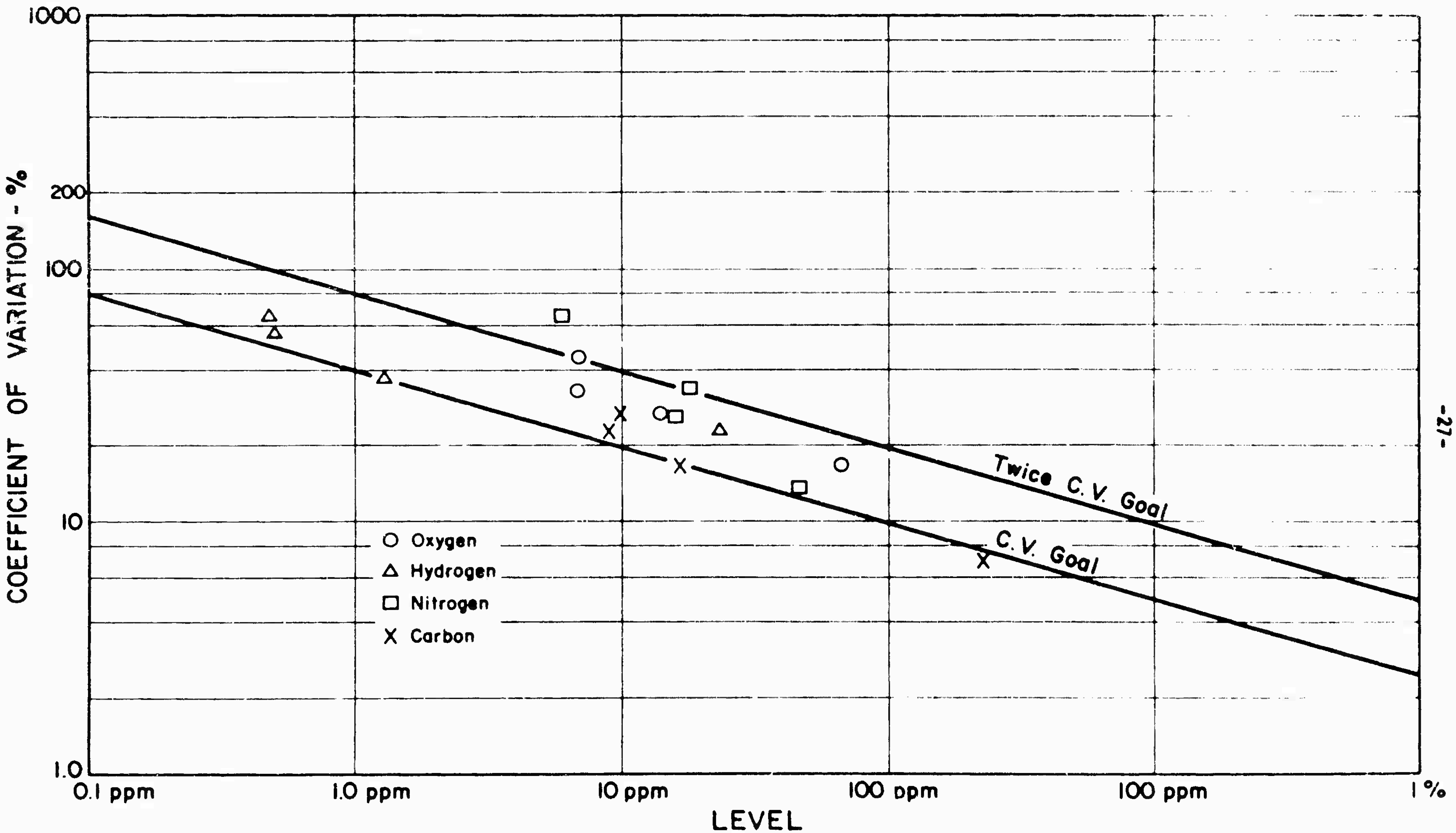

FIGURE 2. ROUND ROBIN NUMBER 2 SELECTED RESULTS

(75% retention of data)

Improvement in the precision of determinations made in round robin #2 is evident in nearly all cases. Using selected values, the coefficient of variation goal has been attained or narrowly missed in the case of carbon and hydrogen determinations. Selected oxygen values yield a value equal to or less than twice the coefficient of variation goal.

Many laboratories reported difficulties in following the procedure for nitrogen and fewer results were reported for this determination than for any of the others. Several of the values reported had been obtained by modifying the dissolution step of the procedure, and although laboratories showed fair agreement on alloy FS-85, it is apparent that the dissolution method given in the ground rules is not satisfactory. This method was arbitrarily selected after a task force organized by the subpanel failed to resolve questions regarding the method for nitrogen, and it was recognized in advance that difficulties existed.

Round robin #2 also produced some significant shifts in average values. This is most noticeable in the oxygen data where average values shifted from 20% to 40% of the average reported in round robin #1. Carbon averages for FS-85 and tungsten also shifted considerably when all values are considered, the change in tungsten data being quite dramatic. All changes were to lower values, except the value for oxygen in FS-85, which rose from 53 ppm to 68 ppm.

Results of round robin #2 were discussed at a meeting of the subpanel and participants on March 11, 1964, resulting in the following conclusions and recommendations:

1. Further development of a nitrogen procedure is needed. This calls for a research effort beyond the activity of this group.
2. The determination of hydrogen seems to be generally satisfactory.

3. The determination of carbon is generally satisfactory. New developments in instruments may change the carbon picture radically and more work with existing equipment would probably not be fruitful.

4. Shifting oxygen results suggest the possibility of inhomogeneous samples (especially FS-85). An abbreviated round robin #3 involving oxygen determinations in random samples of FS-85 and TZM was recommended.

ROUND ROBIN #3

In view of the suspicion of inhomogeneity, in particular the FS-85 and TZM reference alloys, a third round robin with limited participation was initiated to establish the homogeneity of these two materials. In this round robin, six samples of each of the two alloys were analyzed for oxygen by each participant, under the same ground rules established for round robin #2. The samples were taken from different sections of the bar stock, distributed to participants in a random fashion, but carefully catalogued as to original position.

A. Results and Discussion - Round Robin #3

Results are given in Tables XIV and XV.

TABLE XIV

Round Robin #3, Oxygen Content (ppm) Measurements of TZM by Participant and Rod

	Rod M-22-A			Rod M-22-B		
Participant	Avg.	Range	No.	Avg.	Range	No.
F	4.9	1.6	3	5.0	0.6	2
H	5.2	2.1	3	4.6	1.9	3
I	4.7	0.9	3	4.8	0.9	3
J	5.5	1.0	3	5.8	1.4	3
O	2.2	0.8	3	1.7	0.5	3
P	6.3	5.0	3	7.3	4.0	3
Q	8.2	4.6	3	14.6	23.3	3
C	4.5	0.8	3	-	-	-
	6.8	6.2	3			
E	8.9	8.0	3	-	-	-
D	8.0	6.0	3	15.3	2.0	3
				14.7	4.0	3
T	-	-	-	5.0	6.0	3
				6.3	1.0	3
V	-	-	-	11.3	2.0	3
				10.0	3.0	3
W	-	-	-	10.7	4.0	3
				17.7	4.0	3

TABLE XV

Round Robin #3, Oxygen Content (ppm) Measurements of FS-85 by Participant and Rod

	Rod NA-10-A			Rod NA-10-C		
Participant	Avg.	Range	No.	Avg.	Range	No.
F	52.2	3.6	3	53.9	1.8	2
H	92.0	3.0	3	87.0	5.0	3
N	57.0	14.0	3	53.0	6.0	3
O	68.0	10.0	3	57.7	4.0	3
P	77.7	14.0	3	77.3	6.0	3
Q	82.7	6.5	3	84.2	26.4	3
W	59.5	29.0	4	53.0	26.0	4
X	61.4	4.5	3	57.1	8.7	3
C	49.0	0.0	2	-	-	-
	49.7	1.0	3			
I	56.0	6.0	3	-	-	-
	54.3	1.0	3			
V	57.7	14.0	3	-	-	-
	55.7	8.0	3			
D	-	-	-	65.3	26.0	3
				67.0	14.0	3
T	-	-	-	56.5	1.0	2
				49.3	12.0	3
E	-	-	-	119.3	31.0	3
				113.5	23.0	2
J	-	-	-	65.7	1.0	3
				64.0	4.0	3

The results produced in round robin #3 are quite similar, in some respects, to the data produced in round robin #2.

	Oxygen (ppm)			
Alloy	FS-85		TZM	
Round Robin Number	2	3	2	3
Average	68	67	9.2	7.8
Standard Deviation	17.1	18.6	6.15	3.99
Coef. of Variation	25.2%	27.8	66.9%	51.%
Number of Values	18	15	18	13

Looking for discrepancies in average values reported for the two sections of FS-85, statistical analysis indicates a small but significant difference between NA-10-A and NA-10-C. However, one finds only two laboratories (O and W) with results varying by more than 5 ppm. Laboratory W shows a wide spread of results for each individual section, 43-72 ppm for one and 40-66 ppm for the other. The inhomogeneity is apparently quite minor.

Considering the data for TZM in the same manner, one finds only 3 laboratories out of 13 with results varying from one section to another by more than 2 ppm (laboratories C, Q and W). Of these three, laboratory C (showing only a 2.3 ppm spread between sections) has a rather large range on one section (4.1-10.3 ppm) and laboratory Q has one very large value on one section (29.6 ppm) giving a wide spread on that sample. Again, only one laboratory (W) has data indicating a difference between sections greater than 2 ppm. There is no concrete evidence of inhomogeneity in this set of data.

IV. SUMMARY AND CONCLUSIONS

A. Major Alloying Constituents

The results of round robin #1, conducted with a minimum of ground rules, indicate that no serious problems are encountered in the determination of the alloying elements, with the possible exception of Zr in FS-85. A summary of the data is given in the following table. These values were computed after elimination of about 1/4 of the outlying results, and therefore represent a selected 75% of the reporting laboratories for each determination:

	FS-85			TZM		T-111	
	Ta	W	Zr	Ti	Zr	Hf	W
Avg.	27.67%	10.11%	0.92%	0.50%	0.089%	1.75%	7.88%
Std. Dev.	0.67	0.22	0.092	0.013	0.0055	0.09	0.21
Coef.of Var.	2.4	2.2	10.0	2.6	6.2	5.1	2.7

Since the specification of alloying constitutents must be practically made with a degree of latitude, the above interlaboratory agreement is felt to be adequate for most purposes, except possibly for the determination of Zr in FS-85. A coefficient of variation of 10% at the 1.0% level is rather high, and borderline even for practical control of alloy composition. Part of this variation may be due to inhomogeneity in the reference material (see Table I).

Methods used for determination of the alloying constituents included wet chemical as well as emission and x-ray spectrography, and the agreement obtained indicates that all of these are adequate for the purpose at hand. With no standards available, each laboratory using empirical procedures obviously had to prepare its own standards. Variation in standardization would be reflected in interlaboratory variance. No attempt is made to stipulate preferred methods for the alloying constituents on the basis of the round robin results.

B. Interstitials

The determination of 230 ppm of carbon in TZM presented no problems and attention is directed toward the determination of low levels of interstitials in the refractory alloys. The results of round robin #2 (retention of 75% of data) are summarized as follows:

	Carbon				Oxygen			
	W	T-111	FS-85	TZM	W	T-111	FS-85	TZM
Avg. (ppm)	9.1	17	10	--	7.3	14	68	7.1
Std. Dev. (ppm)	2.12	2.82	2.74	--	3.42	3.85	11.5	2.44
Coef. of Var.(%)	23.4	16.6	27.4	--	46.9	26.9	16.9	34.4

	Nitrogen				Hydrogen			
Avg. (ppm)	6.3	18	43	16	0.47	24	1.3	0.49
Std.Dev. (ppm)	4.09	6.25	5.84	4.25	0.30	5.81	0.51	0.28
Coef. of Var.(%)	65.0	34.7	13.6	26.6	63.9	24.2	39.2	57.2

These results may be compared with the conclusions derived from the survey conducted by the analytical techniques subpanel in 1961 (Report MAB-178-M), summarized as follows:

	O ppm	N ppm	C ppm	H ppm
Area 1	100 and up	10 and up	10 and up	20 and up
Area 2	10-100	5-10	5-10	5-20
Area 3	1-10	1-5	1-5	0.1-5

Area 1 Generally satisfactory in the hands of competent people with good equipment.

Area 2 Satisfactory for some materials. Further validation needed in most instances.

Area 3 Generally beyond meaningful application at present. Existing equipment for oxygen and hydrogen has required sensitivity. New approaches or considerable refinement of existing ones needed for nitrogen and carbon.

The goal coefficient of variation of 20% at 10 ppm of carbon was equaled or nearly equaled in W, FS-85, and T-111 which confirms the impression that this determination can be made satisfactorily by methods and equipment now commonly used. These include Leco induction as well as resistance furnaces with conductometric readout. Furthermore, new developments in methods for carbon are imminent which promise to further extend the sensitivity of this determination. Therefore, no problem is foreseen for levels of carbon now encountered in commercial refractory alloys.

The determination of very low levels of hydrogen was in a surprisingly better state than expected using the hot extraction method. This technique seems capable of furnishing a reliable hydrogen determination at levels of the order of 1 ppm. No problems in analysis for hydrogen are indicated.

Interlaboratory agreement in the determination of low levels of oxygen and nitrogen with existing techniques and equipment was much less satisfactory than for carbon and hydrogen. Nevertheless, the level of agreement attained at 10 ppm and above is probably adequate for most practical purposes. This is true in spite of the fact that a wide variety of equipment and operating set-ups is represented, and operating practices differ from laboratory to laboratory, as indicated by blank values ranging from 1-60 micrograms. Undoubtedly, better agreement could be achieved by further standardization of procedures. The basic accuracy of the fusion methods is confirmed by agreement with activation analysis results given in Table XII.

Below 10 ppm, and, for research or other critical purposes at higher concentration levels, the indicated coefficient of variation of twice the goal coefficient is undesirably high. The vacuum and inert gas fusion methods in use for the determination of oxygen, and Kjeldahl method for nitrogen are inherently capable of the desired sensitivity. Reasons for lack of agreement reside in details of the analytical procedures. At low levels of oxygen, the surface oxide on specimens leads to high results. The amount of surface oxide present will vary widely with minor changes in surface preparation. Another cause for poor agreement in oxygen analysis is high and variable vacuum or inert gas fusion blanks.

Difficulty with the nitrogen determination centered aound the problem of sample dissolution. Excessive time required to dissolve samples leads to contamination from the atmosphere. Refractory nitrides such as ZrN, which occur in many of these alloys, may resist complete solution. Once the sample is in solution, the isolation and measurement of nitrogen can be easily and accurately accomplished.

As previously mentioned, a task force under W. F. Harris, with Dr. D. Schaffer assisting in the design of the experiment and statistical analysis of the results, was established by the Subpanel.* It concluded, after a study of the method for nitrogen, that none of the methods investigated were adequate for dissolving massive samples. The method of sample dissolution specified in the ground rules for round robin #2, (p. 20) was, therefore, arbitrarily selected, and many participants found this to be unsatisfactory. Rapid decomposition of H_2O_2 in Pt dishes was mentioned as a cause of difficulty in solution. This was avoided by one participant by placing the sample in a heavy-walled polyethylene bottle with 10 ml HF, 10 ml H_2O, and 2 ml H_2O_2. The bottle is sealed and cooked at 70°C for tungsten and 90-95°C for the other materials. A second addition of 2 ml H_2O_2 may be necessary. This technique conserves reagent and keeps blanks at 3-4 micrograms. The problem of dissolving all nitrides in refractory alloys was discussed. Some laboratories routinely filter the solution and fuse the residue even if no particles are visible.

The conclusions derived from the 1961 survey require some modification, therefore, in light of the round-robin results. It appears that the hydrogen and carbon analyses are in better shape than indicated in the table on p. 34, and hydrogen > 1 ppm and carbon > 10 ppm should be placed in area 1,

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*Additional Members: F. P. Byrne, Russell Bossler, Everett W. Hobart, T. D. McKinley, and D. M. Mortimore.

i.e., generally satisfactory in the hands of competent people with good equipment. The status of the nitrogen analysis is, however, poorer than that indicated and probably similar to that of oxygen, which is approximately correctly given in the table.

C. Recommendations for Future Work

The principal recommendations for future work are concerned with analysis for oxygen and nitrogen at low levels. Continued research to improve the precision of the vacuum and inert gas fusion methods for levels of oxygen below 10 ppm is recommended. Attention should be given to reducing the oxygen content of the blank, as well as to establishing optimum sample and bath sizes for precision at low levels. The investigation of promising new methods for the determination of oxygen and nitrogen in concentrations below 10 ppm should be supported.* For example, it would be desirable to explore the determination of O in low-oxygen materials by hard gamma irradiation which produces O^{15}. Oxygen 15 decays with a half-life of 2.1 minutes which permits cleaning of the surface before counting and thus allows determination of the core oxygen without interference from adventitious surface oxide.

Methods that assure the rapid and complete solution of massive samples for the determination of nitrogen need to be developed and proven. Special attention should be given to the disposition of refractory nitrides in alloys, and their influence upon the accuracy of chemical analysis.

Finally, it should be mentioned that remaining quantities of the reference alloys used in those studies have been turned over to the National Bureau of Standards and are available for use in the future by qualified organizations wishing to check their methods of analysis. The compositions of these alloys are given on Page 2.

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*Samples of the reference alloys were distributed late in this program to a number of laboratories for mass-spectrometric analysis of the content of interstitials. At the time of writing results of this study had not yet been received. These will be forwarded to D. L. Chase of the Defense Metals Information Center at Battelle Memorial Institute, Columbus, Ohio.

APPENDIX I

LETTER OF ASSIGNMENT

OFFICE OF THE DIRECTOR OF DEFENSE RESEARCH AND ENGINEERING

Washington 25, D. C.

June 18, 1959

Dear Dr. Bronk:

The Bureau of Aeronautics has initiated a Refractory Metals Sheet Rolling Program, expansion of which is expected both with Bureau of Aeronautics funds and expected supplemental funds from DOD.

Because of the importance and complexity of the program and the many diversified interests in it, the Bureau of Aeronautics has requested the assistance of the Materials Advisory Board in the form of an Advisory Committee, to function in a manner similar to that of the advisory group in the Bureau of Aeronautics for the Titanium Sheet Program.

It is requested that the above committee be established after consultation with the Bureau of Aeronautics as to details. It is understood that this office will be kept advised of the progress of the work under this assignment.

It is understood that this assignment is acceptable to the National Academy of Sciences - National Research Council, and will not require funds beyond the current contract appropriations.

Sincerely yours,

J. R. Townsend
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COOPERATIVE ANALYSIS PROGRAM ON REFRACTORY METAL ALLOYS

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13. ABSTRACT

As a part of the Refractory Metals Sheet Rolling Program, reference materials (unalloyed W, T-111 Ta, FS-85 Cb, and TZM Mo) were prepared and analyzed by 25 cooperating laboratories. No serious problems were encountered in determining alloying elements. Hydrogen and carbon determinations could be made satisfactorily at the levels encountered, but agreement on oxygen and nitrogen was not satisfactory below the 10 ppm level. Recommendations for research to solve remaining problems are offered.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Chemical Analysis						
Refractory Metals						
Columbium						
Tantalum						
Molybdenum						
Tungsten						
Oxygen						
Carbon						
Nitrogen						
Hydrogen						

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