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# CANADA

# DEPARTMENT OF MINES AND TECHNICAL SURVEYS

**OTTAWA** 

MINES BRANCH INVESTIGATION REPORT IR 62-23

# DETERMINATION OF HYDROGEN, OXYGEN AND NITROGEN IN MOLYBDENUM, NIOBIUM, TANTALUM AND TUNGSTEN

G. SMELSKY & N. S. SPENCE

by

PHYSICAL METALLURGY DIVISION

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- - -

## SUMMARY OF RESULTS

The work described in this report was part of an inter-laboratory investigation of gas analysis techniques organized by the Structures and Materials Panel of the Advisory Group for Aeronautical Research and Development (AGARD), which is a branch of NATO.

Samples of molybdenum, niobium, tantalum and tungsten from different sources and in a variety of forms, were analysed for hydrogen, nitrogen and oxygen using two vacuum fusion units. Besides the analytical results, details are given of equipment and procedures. It has been found that analysis of certain samples by conventional methods may give different results depending upon the gas extraction technique employed.

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#### IN TRODUCTION

The vacuum fusion and sub-fusion methods of gas analysis have been widely applied to gas-metal studies and are well documented in the literature (1-9).

The principles of the methods are simple. In vacuum fusion the sample is melted in a graphite crucible, and at high temperatures the metal oxides and nitrides decompose in the presence of carbon forming carbon monoxide and nitrogen. At the same time as the reaction with carbon is taking place, the hydrogen, oxygen and nitrogen in solution in the metal are evolved. Various liquid-metal baths are used to achieve intimate contact with the carbon as well as to assist with the decomposition of the sample.

The sub-fusion method, otherwise known as the hot extraction method, may be employed with or without a graphite crucible but for analysis of most refractory metals the techniques and apparatus require, are basically similar to that of vacuum fusion. By employment of suitable reaction conditions and high vacuum for rapid removal and transfer of gas, both methods permit quantitative determination of the gases contained in a sample.

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Hydrogen, oxygen and nitrogen can be determined in niobium, molybdenum, tantalum and tungsten by different gas extraction techniques. Hydrogen, since it is readily diffusible, can be extracted at sub-fusion temperatures. Oxygen may be extracted from some refractory metals by heating under vacuum in the presence of carbon to elevated, but sub-fusion, temperatures. However, complete extraction of oxygen and nitrogen generally requires fusion of the sample and suitable reaction conditions.

The vacuum fusion units described in this report have been in use for a number of years for the determination of gases in a wide range of metals and alloys. Of the metals niobium, molybdenum, tantalum and tungsten, only niobium and tantalum had been analysed previously. The analytical techniques that were developed could not be verified because comparative analysis figures were not available for the material analysed.

The work described in this report was part of a test program organized by AGARD (under the auspices of NATO) for the purpose of evaluating methods of vacuum fusion gas analysis of niobium, molybdenum, tantalum and tungsten through analysing samples of these metals provided by sources in Belgium, France, the United Kingdom and the United States of America. The time limit set for completion of the test program made it impracticable to investigate new analytical methods and the work was perforce confined to current procedures.

#### DESCRIPTION OF SAMPLES

Details of the samples submitted by the different

countries participating in the programme are given in Table 1.

#### TABLE 1

#### Details of Samples Submitted for Gas Analysis

#### Identification

#### Form of Sample

France,	molybdenum 2
United K	ingdom, molybdenum 2
United S	tates, molybdenum M2C

Belgium, niobium 9N France, niobium 4 United Kingdom, niobium 2 United States, niobium M3B United States, niobium MSG United States, niobium P4G

Belgium, tantalum 2 France, tantalum 2 United Kingdom, tantalum 2 United States, tantalum M3A United States, tantalum M3B

France, tungsten 2 United Kingdom, tungsten 2 United States, tungsten M2D United States, tungsten M3H rod, 10 mm dia x 125 mm rod, 0.6 mm dia x 30 mm rod, 16 mm dia x 5 mm

rod, 56 mm dia x 8 mm
14 mm x 14 mm x 32 mm
rod, 0.6 mm dia x 36 mm
4.5 mm x 9 mm x 85 mm
rod, 37 mm dia x 19 mm
small pellets approximately
0.2-1.0 mm dia

rod, 40 mm dia x 10 mm 8 mm x 8 mm x 76 mm rod, 0.6 mm dia x 19 mm 0.5 mm x 70 mm x 212 mm 3.5 mm x 8 mm x 137 mm

rod, 10 mm dia x 64 mm rod, 0.6 mm dia x 165 mm 13 mm x 14 mm x 35 mm rod, 8 mm dia x 120 mm

#### SAMPLING

In the determination of gas content of metals both the initial sampling procedure as well as the final sample preparation immediately before analysis play important roles in obtaining accurate results. In the present work it was necessarily assumed that the samples supplied were truly representative of the parent material. The sample preparation procedure applied to the niobium, molybdenum and tantalum metals was to cut analytical samples by means of a hand saw. The specimens were then abraded with a file and ringed in pure benzene and thoroughly dried. The tungsten samples were prepared by breaking the material to size in a vise and selecting the required amount from the fresh clean inner material. Benzene rinsing was avoided since the more porous nature of this material might lead to absorption and retention of the solvent and in any case, the freshly broken surfaces were uncontaminated by handling or manipulation. All samples were prepared immediately before analysis and were placed in the apparatus with the minimum of delay. OUTLINE OF GAS EXTRACTION TECHNIQUES

Vacuum fusion and sub-fusion (hot extraction) methods of gas analysis were used throughout the investigation but various

techniques were employed and these are listed in Table 2.

# TABLE 2

#### Gas Extraction Techniques

Method	Temperature	Application
A Hot Extraction	1850-2050°C (3360-3420°F)	To establish the base level gas content, recoverable by simple extraction.
B Platinum bath	1900°C (3450°F)	To obtain comparative figures at high fusion temperatures.
C Iron bath	1650°C (3000°F)	To determine the effective- ness of iron as a fusion medium.
D Iron-tin bath	1650°C (3000°F)	To determine the effect of tin addition with respect to gas recovery.
E Tin flux	Tin added with sa with any of the m	ample. Used in conjunction ethods A, B, C or D.

The niobium, molybdenum, tantalum and tungsten samples were, in general, analysed in analytical runs independently set up for each metal.

Out-gassing and pre-analytical preparations were carried out in the usual manner and satisfactorily low blank values were achieved before and during the analyses. Actual analysis of the gases extracted from a sample was carried out by conventional methods, the reliability of which had been well-established in earlier work.

#### RESULTS

The results of the gas analyses are given in Tables 3 to 5. The gas extraction methods used in the analysis of each sample are indicated in the "Method" column by capital letters which correspond to the letters listed in Table 2. The values obtained from the various extraction methods agreed as regards order of magnitude except for three oxygen determinations which are indicated by the small letters in the "O<sub>2</sub> Content" column of Table 4; these three determinations are reviewed under "Discussion of Results". The samples are identified in the tables as BEL (Belgium), FR (France), UK

(United Kingdom) or US (United States of America).

# TABLE 3

Results of Hydrogen Analyses of Molybdenum, Niobium, Tantalum and Tungsten

San	nple	H2 Content	Standard	Number of	Method
Identi	fication	Average (wt %)	Deviation	Analyses	(see Table 2)
FR	Mo 2	0.00079	0.00036	12	A, B, C, DE
UK	Mo 2	0.00009	0.000035	18	A, B, C, DE
US	Mo M2C	0.00011	0.00005	10	A, B, C, DE
BEL	Nb 9N	0.00008	0.00005	14	B
FR	Nb 4	0.00009	0.00006	6	B
UK	Nb 2	0.00041	0.00004	11	A,B
US	Nb M3B	0.00011	0.00004	6	A,B
US	Nb MSG	0.00020	0.00006	7	B
US	Nb P4G	0.0049	0.0003	5	AE,BE
BEL	Ta 2	0.00004	$\begin{array}{c} 0.00003 \\ 0.00004 \\ 0.00003 \\ 0.00001 \\ 0.000015 \end{array}$	7	A, B, DE
FR	Ta 2	0.00004		17	A, B, DE
UK	Ta 2	0.00012		15	A, B, AE, DE
US	Ta M3A	0.00005		6	A, B, DE
US	Ta M3B	0.00002		11	A, B, AE, DE
FR	W 2	0.00006	0.00002	5	A, B
UK	W 2	0.00008	0.00003	7	A, B, DE
US	W M2D	0.00015	0.00004	7	A, B, DE
US	W M3H	0.00007	0.00002	5	A, B, DE

Results	of	Oxygen	Analyses	3 0	f Molybdenum,	Niobium,	Tantalum
1		· · ,	·	nd	Tungsten		· .

TABLE 4

Sample Identification	O2 Content Average (wt %)	Standard Deviation	Number of Analyses	Method (see Table 2)
FD Ma2	0 0035 (5)	0 0015	13	ABCDE
IK Mo2	0.0035 (a)	0.0012	15	A.B.C.DE
US Mo M2	C 0.0007	0.00015	9	A,B,C,DE
BEL Nb 9N	0.0012	0.0003	10	В
FR Nb 4	0.0062	0.0010	· 9 ·	B
UK Nb 2	0.0019	0.00042	9	Α
US Nb M3E	3 0.017	0.0046	17	A,B
US Nb MSC	. 0.035	0,0024	6	B
US Nb P4C	0.012	0.0018	. 5	AE,BE
BEL Ta 2	0.00066	0.00021	8	A,B,DE
FR Ta 2	0.0022 (c)	0.0014	17	A, B, DE
UK Ta 2	0.00065	0,0003	12	A,B,AE,DE
US Ta M3A	0.0095	0.0018	9	A,B,DE
US Ta M31	3 0.0037	0.00066	11	A, B, DE
FR W 2	0.00059	0.00012	5	<b>A</b> , B
UK W 2	0.0012	0.00014	4	<b>A</b> , <b>B</b>
US W M2D	0.00083	0.00027	8	A, B, DE
US W M 3H	0.00050	0.00020	5	A, B, DE

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TABLE 5	BLE 5	$\mathbf{E}$	I	.В	A	Τ.
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ICEB	uits of 141	trogen Anaryses	or morybuer	ium, istobiu	m, ramaium
		and	l Tungsten		
Sai	nple	N <sub>2</sub> Content	Standard	Number of	Method
Ident	ification	Average (wt %)	Deviation	Analyses	(see Table 2)
FR	Mo 2	0.00089	0.00057	8	B,C,DE
UK	Mo 2	0.00079	0.00027	16	A,B,C,DE
US	Mo M2C	0.00033	0.00019	8	B,C,DE
BEL	Nb 9N	0.0031	0.00063	12	в
$\mathbf{FR}$	Nb 4	0.0037	0.0014	9	В
UK	Nb 2	0.0032	0.0009	9	В
US	Nb M3B	0.0156	0.0021	7	В
US	Nb MSG	0.00079	0.00016	6	В
US	Nb P4G	0.00044	0.00023	4	AE,BE

0.00011

0.0029

0.00064

0.00043

0.00019

0.00009

0.000083

0.000045

0.000055

B,DE

B,DE

В.

B,DE

A,B

A,B

A,B,DE

A,B,DE

A,B,DE

5

15

8

8

5

4

7

5

5

0.00025

0.0055

0.0023

0.00070

0.0010

0.00005

0.00015

0.00014

0.00015

Annal lange and Martinel and an of Milder NT: -1- ----

#### DISCUSSION OF RESULTS

#### Hydrogen Analyses

BEL Ta 2

FR.

UK

US

US

FR

UK

US

US

Ta 2

Ta 2

W 2

W 2

Ta M3A

Ta M3B

W M2D

W M3H

Good agreement was obtained between the hydrogen

analyses irrespective of the extraction method employed.

# Oxygen Analyses

The consistency of the oxygen results was found to vary with the material, purity of sample and gas extraction technique employed. The average values indicated by the letters (a), (b), and (c) in Table 4 were obtained from individual results which showed more scatter than usual, and the separate averages for the techniques employed were as follows:

- (a) FR Mo 2 Average of following 13 determinations:
  3 hot extraction average 0.0016 wt %
  - 2 platinum bath average 0.0020 wt %
  - 3 iron bath average \* 0030 wt %
  - 5 iron-tin bath (samples enclosed in tin cup) - average 0.0050 wt %.
- (b) UK Mo 2 Average of following 15 determinations:
  6 hot extraction average 0.0018 wt %
  - 3 platinum bath average 0.0043 wt %
  - 3 iron bath average 0.0019 wt %
    3 iron-tin bath (samples enclosed in tin cup)
  - average 0.0038 wt %
- (c) FR Ta 2 Average of following 17 determinations:
  2 hot extraction average 0.0017 wt %
  - 10 platinum bath average 0.0018 wt %
  - 5 iron-tin bath (samples enclosed in tin cup) - average 0.0039 wt %.

The relationship between oxygen recovery and extraction technique for molybdenum, tantalum and tungsten is illustrated by the bar graphs plotted in Figures 1, 2 and 3, respectively. The results are arbitrarily arranged in order of increasing oxygen content as determined by the hot extraction method. It will be noted that the hot extraction technique generally shows lower oxygen recovery than the fusion methods, especially at the higher oxygen contents.

Evaluation of different extraction techniques for oxygen in niobium was not carried out because gas-metal studies done elsewhere<sup>(10)</sup> indicated that oxygen was readily recovered by conventional hot extraction procedures. Earlier work in this laboratory with niobium verified that excellent agreement could be obtained between hot extraction and platinum bath extraction techniques and for this reason it was unnecessary to carry out extensive comparative tests for oxygen analysis of niobium.



Figure I, Relationship Between Oxygen Recovery and Extraction Technique for Molybdenum







Figure 3, Relationship Between Oxygen Recovery and Extraction Technique for Tungsten

# Nitrogen Analyses

Nitrogen is more difficult to determine than hydrogen or oxygen since complete nitrogen recovery appears to require highly mobile and reactive bath conditions which are difficult to maintain by conventional means, and up to this time these problems have not been solved.

The nitrogen results obtained in the present series of analyses generally tend to be erratic and cannot be considered satisfactory, but they are presented for evaluation.

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- 1. "The Determination of Oxygen in Steel (First Report of the Oxygen Sub-Committee) Iron and Steel Institute (1937).
- R.A. Yeaton "The Vacuum Fusion Technique as Applied to the Analysis of Gases in Metals" - Vacuum <u>11(2)</u>, 115-124 (1952).
- H.A. Sloman, C.A. Harvey and O. Kubaschewski "Fundamental Reactions in the Vacuum-Fusion Method and Its Application to the Determination of O<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub> in Mo, Th, Ti, U, V, and Zr" - J. Inst. Metals, 80, 391-407 (1951-52).
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  - G.V. Mikhailov, Z.M. Turovtseva, and R. Sh. Khaltov -"The Determination of Oxygen, Nitrogen and Hydrogen in Molybdenum, Tungsten and Niobium" - Zhurnal Analiticheskoi Knimi, <u>12</u>, 338-341 (1958); Translation, Consultants Bureau Inc., New York.

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  - A. Parker "The Determination of Gases in Metals by the Semi-Micro Vacuum-Fusion Technique" - Special Report No. 68, The Determination of Gases in Metals, Iron and Steel Inst. (1960).
- 10. J. P. Pemsler "Study of Gases in Metals" United States Atomic Energy Commission, NMI-9800 (August 17, 1959).

#### APPENDIX I

#### GAS EXTRACTION TECHNIQUES

In the initial development work, a series of analyses was carried out using different sample weights (approximately 200, 800 and 1000 mg) to determine the completeness of gas extraction.

The final analytical procedures used were those which gave reproducible results from samples of different sizes as determined in two vacuum fusion units, employing different crucible arrangements. Although reproducible results have been obtained in two different units using the procedures described, it should be recognized that this work was carried out without the use of a reference standard and time did not allow thorough investigation of all available techniques on each sample.

#### Hot Extraction

The hot extraction method has been suggested as a routine analytical method for determination of hydrogen and oxygen in molybdenum, tantalum and tungsten<sup>(1)</sup>. Hot extraction provides the most straightforward method of gas extraction and is the least difficult to apply. The advantages of the method relative to others

employing metal baths are that pre-analysis preparation is a minimum, analyses are rapid, crucibles may be re-used, blanks are small and consistent, and there is less likelihood that the

presence of previously analysed samples in the crucible will interfere with extraction.

In hot extraction, gases are extracted by diffusion processes peculiar to the sample, and controlled mainly by its composition and size. Although good agreement in results may be obtained between fusion extraction and hot extraction at low gas contents there may be discrepancies as illustrated in the graphs in Figures 1, 2 and 3, on pages 12, 13 and 14.

#### Procedure

Samples of 0.2 to 1.5 g were dropped into a well-degassed crucible held at 1850-2050 °C (3360-3720 °F). Gas evolution began immediately and continued for 10 to 20 minutes. Due to the speed at which gas was removed from the region of the crucible, gas evolution could not be monitored effectively with a Pirani

 J. E. Fagel, R. F. Witbeck and H. A. Smith - "Determination of Oxygen, Hydrogen and Nitrogen in Refractory Metals" -Analytical Chemistry, 31(6), 1115-1116 (June 1959).

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gauge positioned near the furnace. Completeness of extraction was determined indirectly by measurement of the total gas collected during extraction, and when the increase of pressure per unit time was equal to the blank value it was assumed that extraction was complete. Although longer extraction times were anticipated for molybdenum, tantalum and tungsten, no further significant evolution of gas was noted after 15 minutes and an extraction time of 20 minutes was considered sufficient for accurate analysis. Generally no significant difference in results was noted when extraction was carried out at 1850°, 1950°, or 2050°C (3360°, 3540°, 3720°F) but, on one occasion during a series of molybdenum analyses, higher gas recovery was obtained with samples in direct contact with the crucible in contrast to samples not in direct contact with the crucible. In hot extraction analysis of molybdenum it was observed that a film was deposited on the furnace walls.

#### Platinum Bath

The platinum bath method has been used in the analysis of beryllium, iron, molybdenum, niobium, plutonium, tantalum,

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thorium, titanium, uranium, tungsten and zirconium(2, 3, 4).

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The advantages of the platinum bath are that platinum has a low vapour pressure and remains quite fluid under normal operating procedures so that it provides an excellent medium for investigating high temperature fusion techniques. Unfortunately, the solubility of carbon in liquid platinum is small, and the bath must therefore be highly fluid to achieve complete gas extraction. As the percentage of sample material increases, the bath becomes viscous and eventually turns partially solid, and for this reason the sample-to-bath ratio must be kept low. It has been found that the maximum amount of alloying permissible is about 25% for molybdenum, niobium, tantalum and tungsten.

Another factor to be taken into account when applying platinum bath alloying techniques is that bath surface condition is affected by the addition of sample material. On several occasions

- (2) E. Booth, F. J. Bryant and A. Parker "Developments in the Micro Vacuum-Fusion Method with Particular Reference to the Determination of Oxygen, Nitrogen and Hydrogen in Beryllium, Titanium, Zirconium, Thorium and Uranium" -Atomic Energy Research Establishment A.E.R.E.C/R 1947, Harwell Berks (1956).
- (3) S. J. Bennett and L. C. Covington "Determination of Oxygen in Titanium, Modified Vacuum Fusion Apparatus and Platinum Bath Technique" - Analytical Chemistry 30(3), 363-365 (1958).
- (4) J. E. Still "The Determination of Gases in Metals by Vacuum Fusion" - Special Report No. 68, The Determination of Gases in Metals, Iron and Steel Inst. (1960).

during the initial tests, the bath surface appeared to become viscous even though the sample-to-bath ratio was low. This was attributed to poor miscibility of sample and bath, and to avoid this effect, fresh platinum was added before each sample. The geometry of the crucible may be another factor which affects alloying conditions since greater surface viscosity occurred more readily in baths where the surface-to-volume ratio was low.

In the initial tests, scrap platinum thermocouple wire was used extensively, but in later work high purity platinum in the form of 1/8 inch diameter wire was used. Similar results were obtained from both materials, although the thermocouple wire required longer out-gassing. All platinum was thoroughly degreased before being placed in the apparatus.

#### Procedure

Initially 10-20 g of platinum were dropped into the crucible and degassed for 30 minutes at operating temperature. Before admission of each sample, additional platinum was added to the bath to provide a fresh surface. The platinum was high purity 1/8 inch diameter wire which was cut into pieces weighing about 0.7 g, and several of these pieces were added if required. A 5 minute treatment was sufficient to completely degas the platinum. Bath temperature was maintained at 1900°C (3450°F) and as many as eight 0.3 to 0.9 g samples could be analysed in the bath. Normal extraction time was 15 minutes, but when large samples (>1 g) were used extraction time was extended to

20 minutes.

# Iron Bath

The use of iron for alloying samples is probably the most practiced technique in vacuum fusion analysis. The usual procedure is to melt samples in a 5 to 20 g iron bath held at 1650 °C (3000 °F). In most analyses, samples are melted consecutively, but in cases where poor alloying conditions exist, extra iron may be added alternately with the samples. However, the latter method lengthens analysis time considerably since the added iron must be degassed thoroughly before sample addition.

In previous work with iron baths, attempts to analyse titanium and zirconium gave erratic results and the technique was abandoned in favour of other gas extraction techniques. However, since the iron bath technique is so commonly used, two analysis runs of several 1.2 g molybdenum samples were carried

poorer as samples were added to the bath. High gas recovery

out for comparison. In each case alloying conditions became

was obtained with the first and second samples analysed, but with

additional samples, gas recovery became low and erratic, and visual observation of the bath showed poor surface conditions, including crust formation. Further addition of fresh iron did not appreciably improve this condition. In view of these difficulties, further work by this technique was discontinued.

### Iron-Tin Bath (samples enclosed in tin)

The iron-tin bath, and iron bath methods are quite similar in that iron is used as the alloying base and the operating temperature is the same, namely  $1650 \,^{\circ}\text{C}$  ( $3000 \,^{\circ}\text{F}$ ). Derge<sup>(5)</sup> used the iron-tin bath technique for analysis of titanium and found that a tin addition gave higher gas recovery. Beach and Guldner<sup>(6)</sup> have shown that the iron-tin bath method with molybdenum samples enclosed in tin gives the highest and most reproducible oxygen results when compared to iron, nickel and platinum baths.

In the present investigation it was found that the irontin bath method with samples enclosed in tin gave high oxygen and nitrogen results in certain molybdenum and tantalum samples when compared to other extraction methods.

<sup>(5)</sup> G. Derge - "Oxygen in Titanium" - J. of Metals, <u>1</u>, 31-33 (1949).

 <sup>(6)</sup> A. L. Beach and W. G. Guldner - "The Application of Vacuum Fusion to Gas-Metal Studies" - ASTM Special Tech. Publ. No. 222 (1957).

#### Procedure

High purity vacuum-melted iron (5-20 g) was added to the crucible a few pieces at a time and subsequently degassed until a low blank was obtained. The total time required to completely degas a large bath was of the order of 40 minutes. When the iron bath had been sufficiently degassed at operating temperature, the crucible was allowed to cool for 5 minutes and 0.3 g of bulk tin was added. The tin acted as a crucible conditioner, and if it were not added the first sample was liable to be expelled from the crucible due to the violence of the reaction. The temperature was then raised rapidly and the tin degassed for 10 minutes. Prior to adding the first sample a small amount of iron (<0.5 g) was added to further condition the crucible. The bath was then further degassed for 15 minutes. Samples weighing 0.5 to 1.5 g and enclosed in a 0.4 g tin cup were analysed between alternate additions of fresh iron (each second sample) and extra tin which was added in the form of a representative tin cup during blank determinations. The extraction time was 20 minutes and each iron addition required a further 20 minute degassing.

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Excessive use of tin must be avoided since the tin is evaporated onto the furnace walls and will couple into the inductive field of the coil thus causing arcing. Arcing due to tin condensation was usually encountered after addition of the fifth sample and this effect still persisted even when the quantity of tin was reduced.

This analytical procedure was lengthy and difficult to carry out since considerable care had to be exercised to retain satisfactory fusion conditions.

#### Tin Flux

Tin has been used as a flux medium in the analysis of several metals. Walter's method<sup>(7)</sup> for oxygen analysis of titanium indicates that tin can be very effective in dispersing a sample so that rapid reaction with carbon can occur. In the present analyses of molybdenum and tantalum by iron-tin bath techniques, it was found that tin enhanced oxygen and nitrogen recovery in certain instances. The role of tin is uncertain but observations made during iron-tin bath analytical procedures revealed that when tin was added to the bath, considerable clean-up of the bath surface occurred. Bath surface clean-up was noted on several occasions when tin was added, but after about 3 minutes the bath surface tended to revert back to its original appearance which suggested some surface film formation.

 <sup>(7)</sup> D. I. Walter - "Determination of Oxygen in Titanium" -Analytical Chemistry <u>22</u>, 297-303 (1950).

The tin flux method, with a dry crucible containing graphite chips, was used on a routine basis in this laboratory for analysis of titanium, and this led to the development of the tin flux techniques using only a dry crucible, for analysis of niobium. Using the modified method, analysis of niobium with high gas content gave results which showed excellent agreement with those obtained by hot extraction and platinum bath techniques.

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Previous work indicated that hot extraction and platinum bath techniques would give the same results, therefore the dry crucible-tin flux method was not included in the investigation. It was felt that the use of tin cups generally should be avoided in analysis of low gas content samples since it is difficult to obtain a representative tin cup blank.

One niobium sample (US Nb P4G) was received in the form of small pellets which necessitated use of a tin cup for convenience in handling. This sample was analysed by the dry crucible method. Niobium pellets (0.3 g) were placed in a tin cup weighing 0.4 g. The sample was dropped into a dry crucible held at 2000°C (3630°F) after initial conditioning with a dummy tin cup. Gas extraction was complete within 20 minutes. To check the results obtained by this method similar samples were analysed in a platinum bath at 1900°C (3450°F). The results were in good

agreement.

## APPENDIX II

#### VACUUM FUSION UNITS

The gas analysis units in use in this laboratory were designed and built here and, although their design is not completely novel, it is thought that some features might be of interest in the final evaluation of the results. Two vacuum fusion units of different design were used to carry out the present series of fusion and sub-fusion analyses. In the descriptions that follows the units are identified as "A" and "C".

## Vacuum Fusion "A" Unit

The vacuum fusion "A" unit was brought into operation in 1950 and has proved to be a sound, practical and effective apparatus. As this unit is of a standard type it has been used to check the results obtained with the other vacuum fusion apparatus employed in this work and which incorporates several new features.

#### Vacuum System

The high-vacuum system is all-glass and includes three mercury diffusion pumps and two mechanical pumps. Gas flow is controlled by mercury "U" type cut-off valves, and pressure measurements are made with a multi-scale McLeod

gauge. The mercury levels in the cut-off valves and McLeod

gauge are raised and lowered by differential pressure by means of hand operated stopcocks mounted on atmospheric and vacuum manifolds. The system is illustrated schematically in Figure 1.



## **Furnace Section**

The furnace section is constructed entirely of Pyrex glass. The main assembly, which is permanently connected to the vacuum system with a large diameter gas exit tube, consists of a cold trap (dry-ice),mercury lift, Pirani gauge head and a "T" shaped member on which the sample tubes, optical flat and high temperature furnace are attached. Samples are moved and admitted into the crucible by means of an iron pusher manipulated by a magnet. The glass optical flat through which temperature observations are made is protected from condensed films by a movable stopper. The Pirani gauge, in addition to measuring the static and dynamic pressure, is connected into a controller so that the induction heater can be turned on and off at any preset pressure

providing automatic bake-out and safety control.

The induction heating set used is a 6 KW Ajax mercury spark-gap type having a nominal frequency of 50 Kc/sec. A

variety of work coils and furnace systems can be used with this type of heater since the characteristics are such that the crucible and

furnace dimensions are not especially critical.

A modification of the basic Guldner and  $\text{Beach}^{(1)}$  furnace design is used and is shown in Figure 2.

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<sup>(1)</sup> W. G. Guldner and A. L. Beach - "Vacuum Fusion Furnace for Analysis of Gases in Metals" - Analytical Chemistry 22, 366-367 (1950).







Figure 3. Graphite crucible and Funnel.

Furnace components are installed through the open bottom end of the furnace tube, which is later sealed with an "O" ring and brass piece.

The graphite crucible and funnel, Figure 3 are machined from high grade graphite rod and are supported in the quartz tube with minus 200 mesh spectrographic grade graphite powder. The lower end of the crucible has been provided with thick walls to prevent leakage during prolonged analysis employing iron baths.

With the components and induction heater in use it has been found unnecessary to slit the funnel to achieve low funnel temperatures.

A maximum crucible temperature slightly in excess of 2400°C (4350°F) has been achieved with this system, but normally the temperature is held to a maximum of 2300°C (4170°F) to avoid excessive condensation.

The furnace section is isolated from the analytical section of the apparatus by two mercury "U" type cut-off check valves. The valves enable the furnace section to be opened to atmosphere while the analytical section remains under vacuum.

## Analytical Section

The hydrogen, carbon monoxide and nitrogen recovered from a sample upon heating or melting in the crucible are collected

in the calibrated volume where the total pressure is measured with the McLeod gauge. For this purpose the diffusion pumps (see Figure 1) are in series. The gases are then circulated over hot copper oxide and the cold trap, which is cooled by a dry-ice/ acetone mixture. Hydrogen is thus removed, and the remaining carbon dioxide and nitrogen are pumped back into the calibrated volume for the second pressure measurement. The cycle is then repeated and carbon dioxide is removed in the cold trap cooled by liquid nitrogen. A third and final nitrogen pressure measurement is taken and thus by difference the hydrogen, carbon monoxide and nitrogen pressures can be determined and the gas content of the sample calculated.

Actual analysis of the gases requires 20 minutes and complete analysis of a sample requires 37 to 47 minutes.

# Vacuum Fusion "C" Unit

The vacuum fusion "C" unit is the second vacuum fusion apparatus developed in this laboratory and makes use of simultaneous gas extraction and gas analysis by semi-automatic means to considerably reduce the time formerly taken for similar analyses. An analysis time of 22 minutes for successive analyses of samples has been achieved. During the course of this series of analyses, the original induction heater and furnace assembly which was identical to that employed in the "A" unit, (see page 30) was replaced, and analyses using iron bath techniques were not carried out since there was not time for development of such techniques. In the present series of analyses for molybdenum, niobium, tantalum and tungsten, this unit was employed only for hot extraction and platinum bath techniques.

#### Induction Heater

A Phillips vacuum tube induction heating set with a nominal output of 6 KW at 900 Kc/sec is used to heat the crucible. Induction heating at these high frequencies requires careful selection and arrangement of the coil and crucible since crucible heating characteristics may play an important role in achieving complete gas extraction. No significant difference in results of analyses of the same sample material was noted when compared with those obtained in the other vacuum fusion unit.

#### The Vacuum System

The high-vacuum system is constructed mainly of glass components, the exception being the quartz high temperature furnace. The system comprises three mercury diffusion pumps,

solenoid-operated glass-mercury seal valves, and a mechanical

pump. An auxiliary mechanical pump is used to provide the differential pressure necessary for operation of the McLeod gauge and mercury "U" type check valves.

The system is illustrated in Figure 4, and a drawing of a solenoid value is shown in Figure 5.

1





Figure 5. Solenoid-operated Glass-Mercury Seal Valve.

# Furnace Section

The furnace assembly of this apparatus differs from that of the vacuum fusion "A" unit in that the furnace diffusion pump is capable of maintaining high fore-pressures at high pumping speeds and a different high temperature furnace arrangement is employed. The high temperature furnace is shown in Figure 6.



Inlet

Figure 6. High Temperature Quartz Furnace Vacuum Fusion "C" Unit.

The advantage of high frequency induction heating as distinct from low frequency heating is that small crucibles may be rapidly heated to high temperatures without the complication of insulating powders or heat shields. In practice considerable time is saved due to simple design of components, ease of assembly and routine maintenance.

Crucibles are machined from high purity graphite and are of a simple design as shown in Figure 7. In hot extraction or platinum bath analyses no funnel is required. Crucible temperatures of over 1900°C (3450°F) have been obtained.



Figure 7. Graphite Crucible.

# **Analytical Section**

Actual analysis of the hydrogen, carbon monoxide and nitrogen recovered from a sample is by diffusion of the hydrogen component through a heated palladium tube and differential freezeout of carbon dioxide in a trap cooled by liquid nitrogen after circulation over "Hopcalite" (activated manganese dioxide).

Three pressure measurements are required for determination of hydrogen, carbon monoxide and nitrogen. Hydrogen is measured directly after diffusion through the palladium tube. A second pressure measurement of carbon monoxide plus nitrogen is then taken and, after freeze-out of carbon dioxide, the pressure of nitrogen is determined. Since hydrogen is evolved rapidly from a sample it is determined before complete extraction of the other gases and normally this is done after 8 minutes of extraction. The gas analysis method has proven reliable and accurate and combined with automatic valving procedures has significantly increased efficiency.

GS:NSS:vb

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