AAEC/E352

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

THE DETERMINATION OF OXYGEN IN METALS USING AN IMPULSE HEATING FURNACE EQUIPPED WITH A SAMPLE TRANSFER LOCK

by

L. S. DALE

S. de JONG

J. W. KELLY

R. N. WHITTEM

May 1975

ISBN 0 642 99683 0

AUSTRALIAN ATOMIC ENERGY COMMISSION
RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

THE DETERMINATION OF OXYGEN IN METALS USING AN IMPULSE HEATING FURNACE EQUIPPED WITH A SAMPLE TRANSFER LOCK

by

L.S. DALE
S. de JONG
J.W. KELLY
R.N. WHITTEM

ABSTRACT

An impulse heating furnace has been constructed for the determination of low levels of oxygen down to 100 μg g^{-1} in metals. The furnace is equipped with a sample transfer lock which permits samples to be loaded into outgassed crucibles in a helium atmosphere. As a result, blank levels in the range 2 to 3 μg oxygen are obtained; the modification also results in shorter sample processing time. The apparatus is described, and its suitability for oxygen determinations at these levels has been verified by comparison of results obtained on reference and analysed materials.

National Library of Australia card number and ISBN 0 642 99683 0

The following descriptors have been selected from the INIS Thesaurus to describe the subject content of this report for information retrieval purposes. For further details please refer to IAEA–INIS–12 (INIS: Manual for Indexing) and IAEA–INIS–13 (INIS: Thesaurus) published in Vienna by the International Atomic Energy Agency.

CALIBRATION; ELECTRIC FURNACES; METALS; OFF–GAS SYSTEMS; OPERATION; OXYGEN; QUANTITATIVE CHEMICAL ANALYSIS; REMOTE HANDLING EQUIPMENT; SAMPLE PREPARATION

CONTENTS

1. INTRODUCTION

Several workers [Vasserman & Turovtseva 1965, Goldbeck, Turel & Rodden 1968, Mead 1970] have described impulse heating furnace systems and their application to the determination of gases in metals and refractory compounds. For the analysis of oxygen in metals such as zirconium to levels as low as 100 μg g^{-1}, using samples of about 250 mg, the blank levels of 20 to 30 μg cited by these workers were unacceptably high.

To achieve blank levels of 2 μg of oxygen, a sample/crucible lock was designed to allow the transfer of crucibles and samples under inert atmospheric conditions. With this lock, it was possible to outgas an empty crucible thoroughly in the impulse heater, transfer it to the lock, load the sample and then return it to the heater. A second feature was the provision of evacuation lines to a rotary pump; this avoided lengthy purge times and permitted the rapid detection of any leaks in the system.

A technique of multiple firings for short periods was adopted and found to achieve a good compromise between recovery of oxygen and freedom from crucible disintegration.

2. EXPERIMENTAL

2.1 Apparatus

2.1.1 Impulse heating furnace

The furnace is essentially that described by Vasserman & Turovtseva [1965] with the addition of convex molybdenum-tipped electrodes as described by Goldbeck, Turel & Rodden [1968]. A general view of the apparatus is shown in Figure 1.

2.1.2 Power supply

Current is supplied by a 20 kVA transformer (secondary winding, 7.5 V at 2,670 A). A bank of series resistors (1 kW radiator bars) in the primary winding of the transformer permits selection of lower currents. With normal crucibles, the currents are approximately 1,300, 700 and 400 A for the three settings. Two timers (with ranges of 0 to 30 seconds and 0 to 60 minutes) and a switch to select the timing cycle are required.

2.1.3 Sample transfer lock and sample loading facility

This unit (Figure 2) consists of a vacuum-tight chamber (A) connected to the furnace *via* a ball valve (B) having a 25 mm full bore. A Wilson seal (C) is connected to the chamber through an Edwards' union (D) and mounted in a direct line with the ball valve. A spring clip, attached to a rod which is held in position by the Wilson seal, carries the crucible in and out of the furnace while the system is being purged with helium. Another Wilson seal (E),

located on the lid of the chamber allows another rod and clip device to remove or replace the crucible lid.

Sample loading is accomplished by a sliding bar-seal device (F) similar to that used by Mead [1970]. The sample is placed in a recess in the bar through a hole in the top of the outer casing of the bar seal. The sample is loaded into the crucible by pushing the bar in until it reaches a stop and then turning it through 180°. A tube fixed to the inside of the chamber directs the sample into the open crucible which is positioned under the tube by the crucible holder. A sectional diagram of the device is shown in Figure 3.

2.1.4 Gas chromatograph

A gas chromatograph (Model GC-3AH), Shimadzu Sersakusho Ltd) is used to analyse the extracted gas. Table 1 gives the operating conditions.

2.1.5 Gas collection and interconnection of components

A U-tube, 10 mm dia x 200 mm long, containing a Linde 5A molecular sieve, is used to absorb the extracted gas at liquid nitrogen temperature (Figure 4). A standard gas chromatographic sampling valve (Perkin-Elmer) is used for gas collection and analysis. A flowrate meter is used to set the helium flow (50 $cm^3\ s^{-1}$).

2.1.6 Calibration

Since the thermal conductivities of nitrogen and carbon monoxide are identical, calibration is carried out with nitrogen gas. A one cm^3 standard loop connected to the sampling valve is used to inject nitrogen from a cylinder at a flowrate of 2 $cm^3\ s^{-1}$. Analysis is carried out by measuring the area of the carbon monoxide peak for the sample and comparing this with the area of the peak obtained from the loop injection.

2.2 Procedures

2.2.1 Start-up

When the apparatus is not in use, the furnace is kept under vacuum and the collection column is kept dry with a heating mantle. The apparatus is made operational by:

(i) establishing the helium flow to the gas chromatograph and switching on the detector system;

(ii) isolating the furnace from the vacuum rotary pump and setting the helium flow to the required level; and

(iii) allowing the system to be purged with helium for about ten minutes.

2.2.2 Outgassing of crucibles

The remote sample-handling chamber is opened to atmosphere by breaking

the seal on the Edwards' union. A crucible and lid, fabricated from Ringsdorff RW IV grade graphite (Figure 5) is then clamped into the holder and placed into the chamber. After remaking the seal, the chamber is then evacuated to a pressure of ~ 1 Pa on the rotary pump. The ball valve is then opened and the crucible and lid are placed between the electrodes of the furnace by advancing the electrode holder through the open bore of the valve. To achieve this, the lower spring-loaded electrode of the furnace is retracted, the crucible is placed in position, and the lower electrode is released. This clamps the crucible between the furnace electrode and permits the holder to be withdrawn leaving the crucible in the firing position. The ball valve is then closed.

When the helium flow stabilises, the crucible is heated for five minutes at 700 A (equivalent to about 1,900°C). The crucible is then heated for three 4-second cycles at 1,200 to 1,400 A (2,600 to 2,700°C). The crucible is cooled for five minutes in the helium flow before opening the ball valve to retrieve the crucible for sample loading.

2.2.3 Sample preparation and loading

Metal samples of approximately 0.25 g mass, and of section 3 x 3 mm by 5 mm long are filed or etched to give a clean surface. The sample is loaded into the recess of the bar-seal loading device and the bar is advanced to the stop position where it is in position for loading.

When the outgassed crucible is withdrawn from the furnace and its lid removed, it is positioned below the delivery tube and the sample is loaded by rotating the bar through 180°. The crucible lid is fitted and the sample is transferred to the furnace and clamped in position. This procedure is carried out in a helium atmosphere. After closing the ball valve, the sample is ready for fusion.

2.2.4 Fusion of sample

The crucible is fired three times for four seconds at 1,200 to 1,400 A. The carbon monoxide formed is purged from the furnace and adsorbed onto the sieve at liquid nitrogen temperature. A five-minute collection time, which includes the firing time, is adequate to adsorb all the liberated gas.

2.2.5 Analysis of extracted gas

After the collection time, the gas is desorbed from the sieve using hot water (80°C). This gas is injected into the gas chromatograph *via* the sampling valve, and analysis is carried out as described in Section 2.1.6.

3. RESULTS

A summary of results for oxygen obtained on analysed and reference metals

is given in Table 2. A problem encountered in testing the validity of the technique at the levels of interest is the lack of certified standards, particularly for zirconium and its alloys. In many cases, samples which had been analysed by other fusion techniques were used. The results obtained by these other techniques are indicated and an accurate value was therefore not available. In such cases, however, acceptable agreement was obtained using the technique described. The results obtained for the US National Bureau of Standards (NBS) titanium reference materials showed very good agreement with the certified values and, overall, the results indicate the validity of the technique for analysing at levels down to 100 $\mu g\ g^{-1}$.

4. DISCUSSION

Sample processing with the remote handling facility is simple and rapid and a complete analysis can be carried out in twenty minutes including the time for crucible outgassing.

A particularly useful feature of the apparatus is the ability to evacuate the system. This speeds up sample processing time, avoids lengthy conditioning procedures and leads to minimum start-up time. It also minimises helium consumption by reducing gas purge times after crucible loading. Contamination of the furnace compartment is also avoided during crucible loading because it can be isolated from the chamber by closing the ball valve which is reopened only when the vacuum in the chamber has been pumped down to background level. Also with the vacuum-tight system, leaks can be readily detected and rectified. This establishes the low blank value which, however, may vary depending on the purity of the helium used.

To prevent the lid becoming cemented to the crucible during outgassing, it was found necessary to make this a loose fit with the cavity of the crucible. This does not appear to affect the recovery of oxygen as carbon monoxide, since the tension of the furnace electrodes is sufficient to create a satisfactory seal between the upper crucible face and the lid.

One disadvantage is that only massive samples can be loaded conveniently. Some moderately successful work has been carried out on powders crimped in platinum foil, but care is needed to ensure that such samples fall freely through the delivery tube and into the crucible. Problems have also been experienced with some irregularly-shaped samples becoming lodged in the delivery tube.

In the initial trials of the apparatus, great difficulties were experienced with crucibles disintegrating if outgassed to a suitably low blank value. This was overcome partly by selecting a grade of graphite with high

flexural strength and suitable adjustment of the tension springs, and partly by adopting the low-temperature outgassing cycle described in Section 2.2.2. Under these conditions, it is possible to use only one sample per crucible.

The results obtained indicate a high recovery as shown by the agreement with the NBS titanium alloy reference materials. The application of the technique to low levels of oxygen is indicated by the results obtained for zirconium iodide bar. To achieve consistently high recoveries, it is essential to replace the molybdenum electrode tips when they become pitted. This problem is evident when the firing current becomes low or erratic.

5. CONCLUSION

The apparatus, together with the procedure adopted, has provided a means for the rapid determination of oxygen in metals. The apparatus requires very little maintenance and can be operated with a minimum start-up time.

6. ACKNOWLEDGEMENTS

The authors wish to thank Mr. A. Payne, Engineering Research Division, for setting up and modifying the transformer and Mr. L. Salter and staff, Operations Division, for construction of the sample transfer lock.

7. REFERENCES

Goldbeck, C.G., Turel, S.P. & Rodden, C.J. [1968] - *Anal. Chem.* 40 : 1393.

Mead, A. [1970] - UKAEA Report. AERE-R6537.

Vasserman, A.M. & Turovtseva, Z.M. [1965] - *Russian J. Anal. Chem.*, 20 : 1390.

TABLE 1

GAS CHROMATOGRAPHIC CONDITIONS FOR THE MEASUREMENT OF CARBON MONOXIDE

Column	4.5 m x 3 mm dia. copper; molecular sieve, Linde 13X
Column Temperature	Ambient
Carrier Gas Flowrate	1 cm^3 s^{-1} He, pressure 195 kPa
Detector	Thermal conductivity detector
Bridge Current	80 mA
Chart Recorder	Bristol Dynamaster 0 - 1.0 mV

TABLE 2

COMPARISON OF OXYGEN RESULTS ON REFERENCE AND ANALYSED SAMPLES USING THE IMPULSE HEATING TECHNIQUE

Sample	Reference/ Analysed Value ($\mu g\ g^{-1}$)	Values Obtained ($\mu g\ g^{-1}$)	Comments
Titanium Alloy NBS SRM No.355	3,031	3,200 2,960 3,190 3,060	Certified standard
Titanium Alloy NBS SRM No.356	1,332	1,330 1,340 1,280 1,280 1,300 1,280 1,310 1,370	Certified standard
Zircaloy-2	1,000	985 1,010 965 950 1,000 980	Nominal value only
Zircaloy-2	960	1,080 1,080 1,120 1,000 1,040 1,000 1,110 960 1,020 1,020	Supplier's certificate of analysis
Zircaloy-2	1,800	1,710	Vacuum fusion result
Zirconium	650	610 620	Vacuum fusion results of 660, 635. Mean taken.
Zirconium (iodide bar)	< 30	< 20 (18) < 20 (13)	Accepted value
Ingot Iron NBS SRM No.1090	491	555 610 555	Certified standard
Stainless Steel NBS SRM No.1091	131	140 142 132	Certified standard

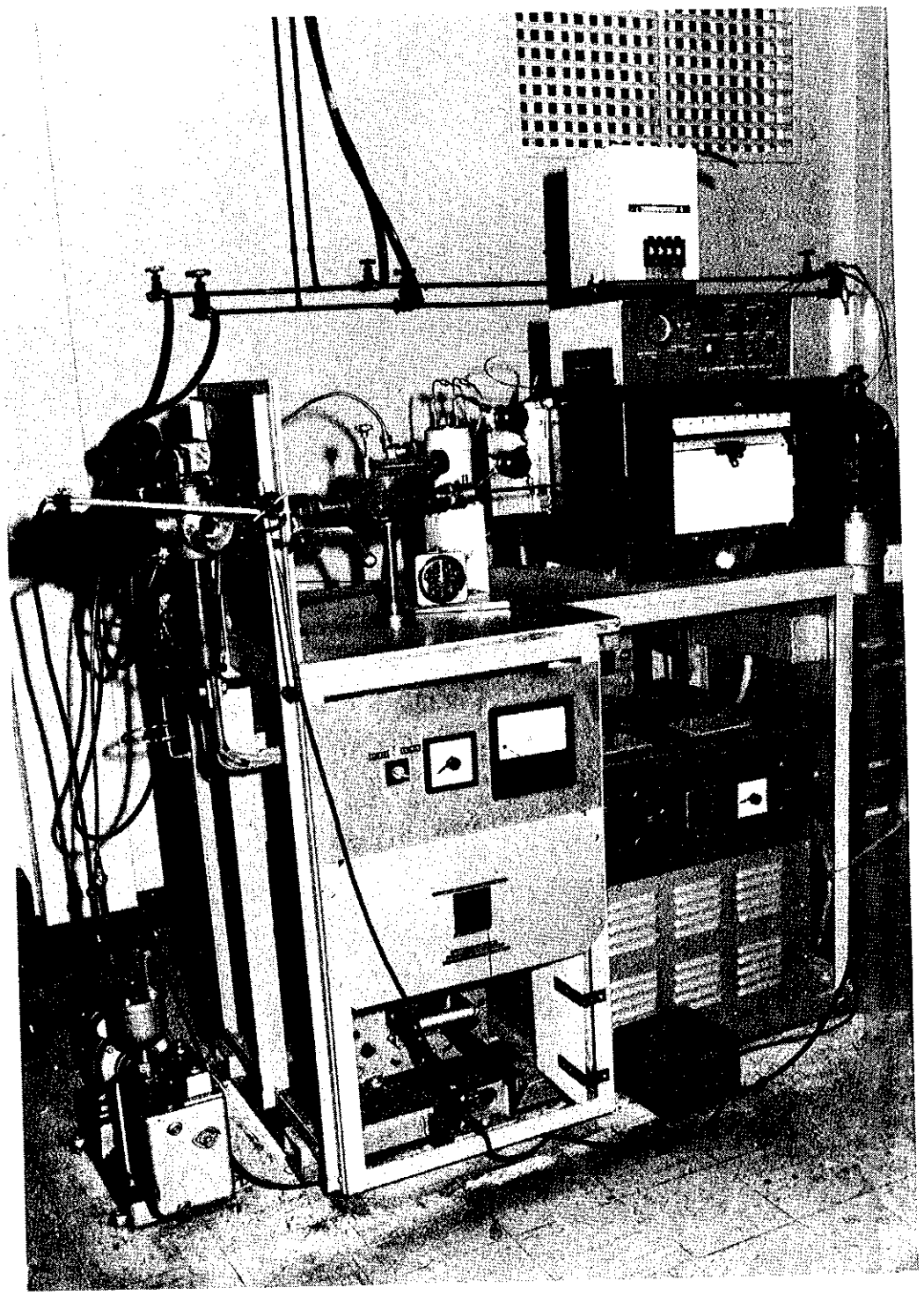


FIGURE 1. GENERAL VIEW OF APPARATUS

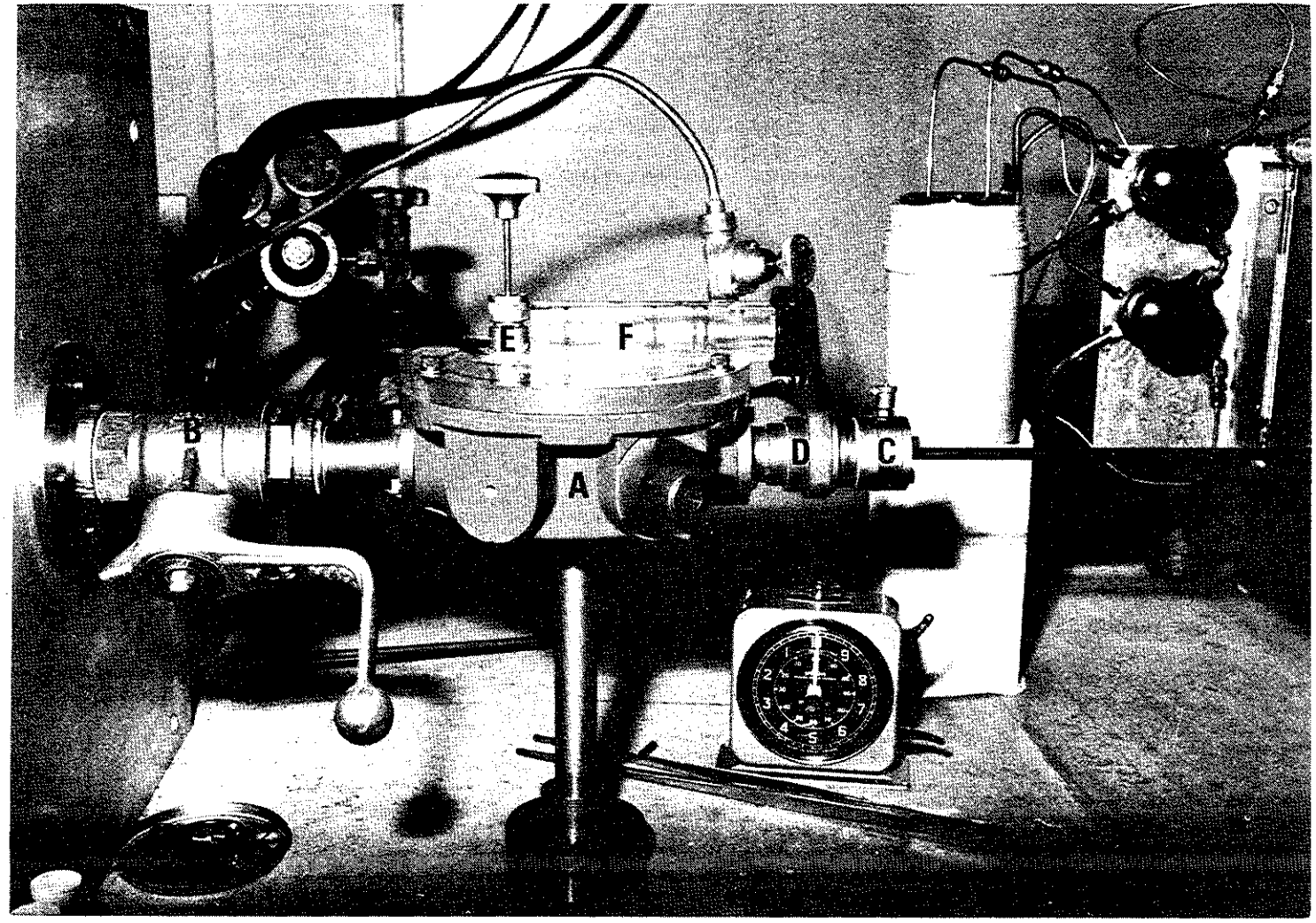


FIGURE 2. REMOTE SAMPLE HANDLING FACILITY

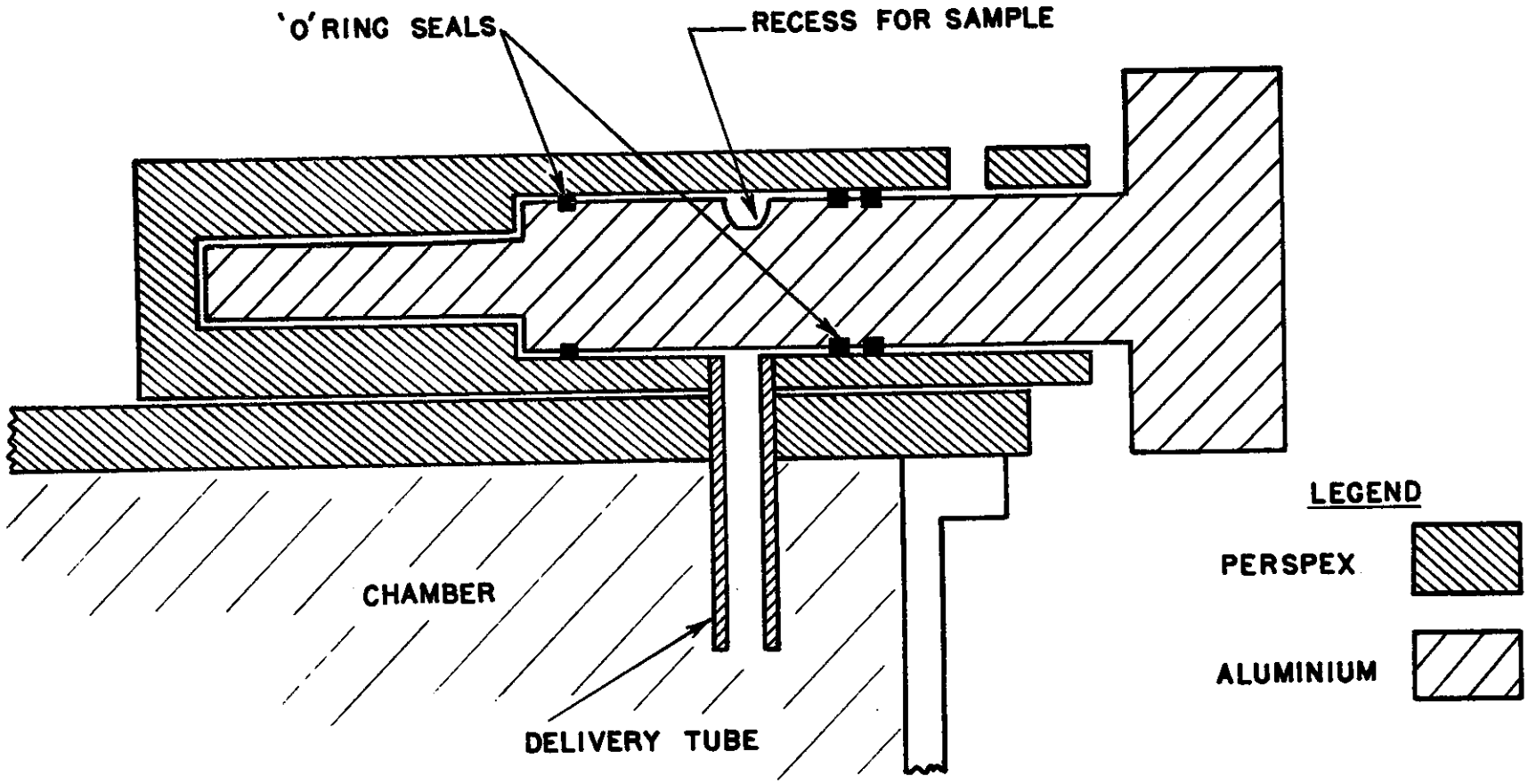


FIGURE 3. SECTIONAL DIAGRAM OF BAR-SEAL LOADING DEVICE

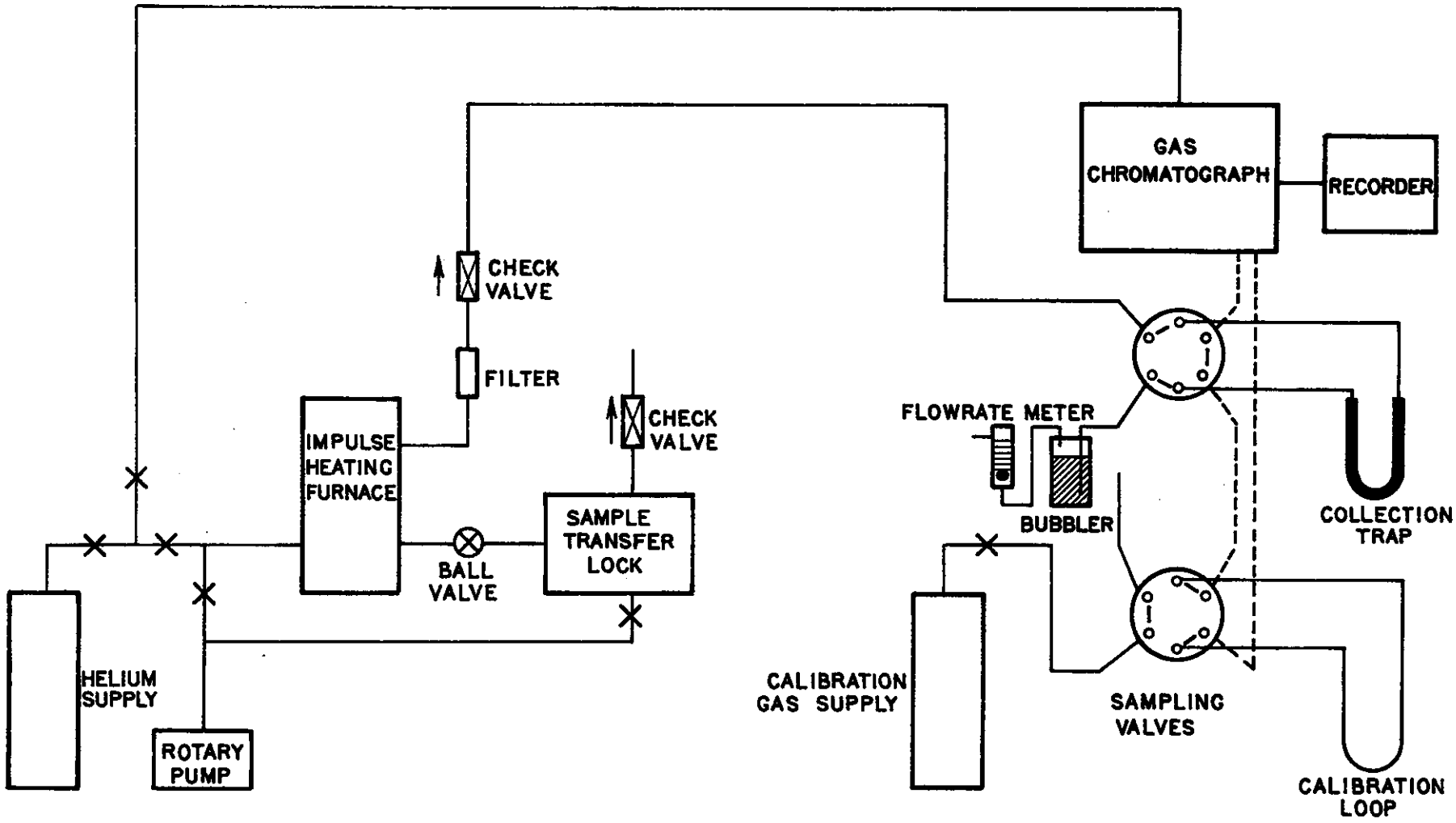
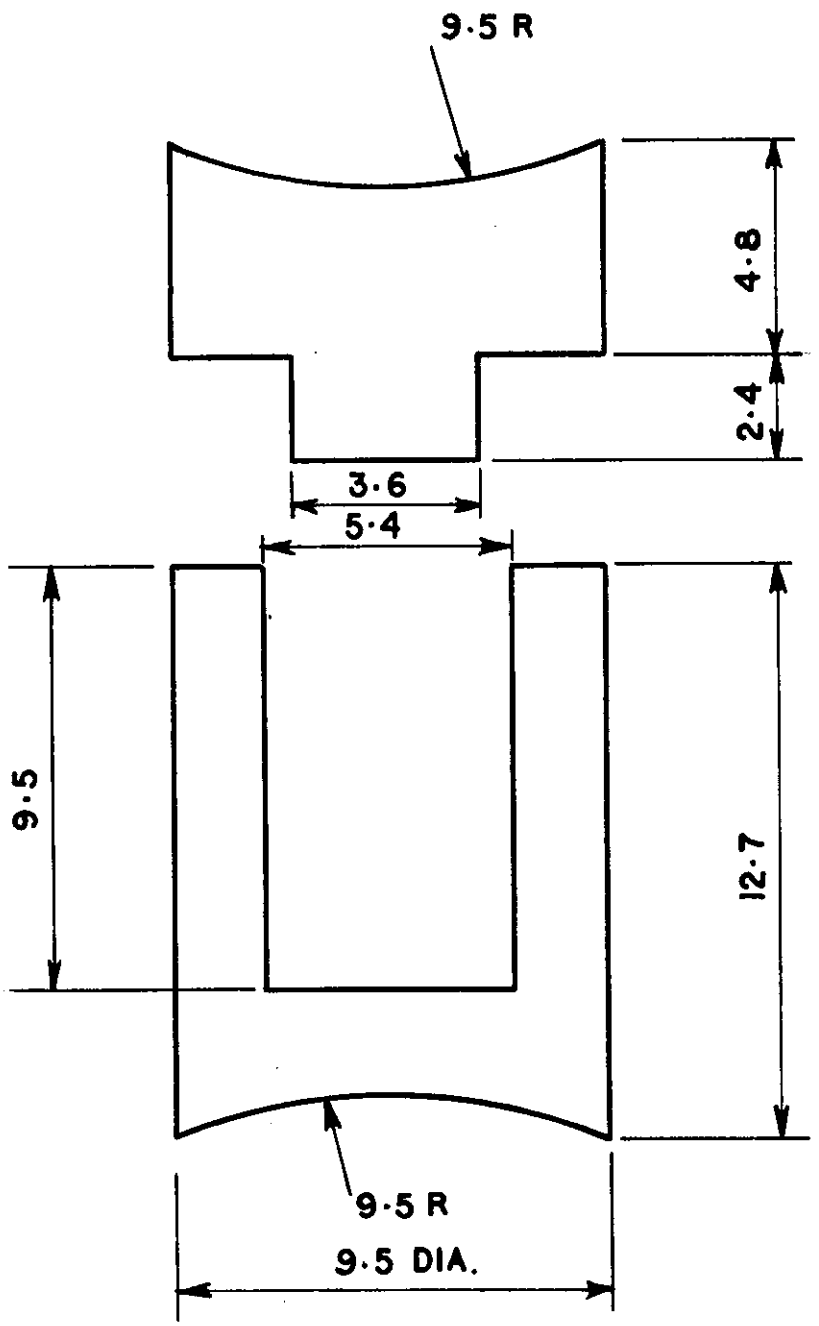


FIGURE 4. SCHEMATIC DIAGRAM OF APPARATUS



ALL DIMENSIONS IN mm

FIGURE 5. CRUCIBLE AND LID