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ABSTRACT

A simple apparatus connected directly to a mass spectrometer enables the fairly rapid determination of hydrogen in metals to be carried out by isotopic equilibration with deuterium. Equilibration conditions have been established from kinetic studies of the exchange process as a function of heating time. Results for titanium metal standards are in excellent agreement with the certified values, relative standard deviations (1σ) ranging from 3.3 per cent at 30 p.p.m. hydrogen to 0.8 per cent at 200 p.p.m.

No standards are available for hydrogen in zirconium, Zircaloy, niobium, vanadium and hafnium. For these metals the equipment has been used to prepare samples with known hydrogen content. Analysis has verified the reliability of the technique.

The sample size requirements are 0.1 to 0.5 g (usually 0.25 g) for the range 1000 to 10 p.p.m. hydrogen.

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INTRODUCTION

The absorption of hydrogen by certain metals has a detrimental effect on their mechanical properties. This effect on titanium, zirconium and their alloys is of particular interest because of their use, in the case of titanium, as construction materials with high strength-weight ratio and heat resistance and, in the case of zirconium, as fuel cladding and pressure tube materials in water-cooled nuclear reactors.

The corrosion of zirconium and its alloys at elevated temperatures in an aqueous environment leads to hydriding which causes embrittlement and fracture failure. This is brought about by the absorption of relatively small amounts of hydrogen by the metal, the saturation solubility of Zircaloy-2 being about 80 p.p.m. at 300°C (Ellis 1968).

To aid research into the corrosion and hydriding of Zircaloys and other similar alloys, analytical procedures of high sensitivity and precision are required in order to correlate these corrosion data with hydrogen content. Both vacuum fusion and vacuum extraction have been used for hydrogen analysis in these materials. The disadvantages of these techniques are long analysis time, complicated vacuum and gas handling equipment and the occurrence of variable readings for blanks. Final analysis usually depends on either mass spectrometry or gas chromatography. Another technique relies on the isotopic exchange which occurs when a metal sample containing hydrogen is heated at an elevated temperature in deuterium gas. A measurement of the isotopic dilution of the gas phase using appropriate equilibration conditions gives the hydrogen content of the sample.

A spectral isotopic-exchange procedure has been described by Zaidel and Petrov (1957) and found to be applicable to various steels, aluminium, zinc and titanium. Ashley and Denovan (1965) used an equilibration procedure for the analysis of titanium and zirconium but determined the isotopic dilution of the gas phase by mass spectrometry. In their method a manifold was used which accommodated a number of equilibration vessels. The manifold was used to evacuate the vessels and fill them with the desired pressure of deuterium. The equilibration could be carried out either with the vessels attached to the manifold or by transferring each vessel in turn to the mass spectrometer and heating. For equilibrations carried out on the manifold it was necessary to reheat the sample to re-evolve the gas when the vessel was transferred to the mass spectrometer for isotopic analysis.

In setting up an isotopic-exchange mass spectrometry procedure in our laboratories, for the determination of hydrogen in metals, we considered the method of Ashley and Denovan but thought it more convenient to construct an equilibration apparatus that could be connected directly to the gas handling system of the mass spectrometer. The advantages lie in the simplicity of the apparatus and the use of the gas handling system of the mass spectrometer to evacuate the vessel and obtain reproducible deuterium gas pressures. No external manifold and pumping equipment is therefore required. The possibility of leaks which could lead to errors in the initial deuterium pressure, a quantity which largely determines the overall precision of the analysis, is also reduced by the use of a diaphragm valve coupling between the equilibration vessel and the mass spectrometer. The apparatus has also facilitate direct measurement of the progress of equilibration in the gas phase, providing data for the optimisation of equilibration conditions.

The procedure has been tested in two ways. Firstly, titanium standards and Zircaloy-2 obtained from the National Bureau of Standards have been analysed and the results compared with the certificated values where available (Section A). Secondly, the equipment has been used to add known amounts of hydrogen to various samples using the mass spectrometer to determine the amount of hydrogen absorbed. Their subsequent analysis by the procedure has been used to evaluate its application to the analysis of zirconium, Zircaloy and other metals (Section B).

SECTION A

ANALYSIS OF NBS TITANIUM METAL STANDARDS AND ZIRCALOY-2

1. EXPERIMENTAL

1.1 Apparatus

The silica equilibration tube of 31 cm^3 capacity is connected through a B14 cone and socket to the inlet of the gas handling system of an AEI type MS3 mass spectrometer. The tube can be isolated from the instrument by a diaphragm valve. Deuterium gas (99 per cent) is admitted from a cylinder through a side arm connected to a mercury doser manometer which sets the pressure. The equilibration tube has a thermocouple attached to it and a small resistance furnace is used for heating. A schematic diagram is shown in Figure 1.

1.2 Procedure

Pieces of metal (0.2 - 0.3 g) are degreased with trichloroethylene and loaded into the equilibration tube. New tubes are preconditioned by heating under vacuum for about one hour at 900°C. After pumping down to the mass spectrometer background ($\sim 10^{-6}$ torr), deuterium is admitted to the system, the pressure (16.5 mm) being fixed by the mercury doser. The equilibration tube is then isolated by closing the valve V1 and the remainder of the gas in the system is transferred to the 2 litre reservoir for a determination of a blank. The sample is heated from ambient temperature to 920°C and kept at this temperature for 10 minutes, the total heating time being 25 minutes. At this point the gas phase is transferred to the reservoir and the H/D ratio determined from measurement of the amplifier outputs for masses 2, 3 and 4. The hydrogen content is calculated from the equation (Zaidel and Petrov 1956):

$$H_2 \text{ (per cent)} = \frac{2\ V\ P_D}{R\ T\ m} \cdot \frac{C_{H_2} - C^1_{H_2}}{C_{D_2} + C^1_{H_2}} \cdot 100 ,$$

where V is the volume (cm^3) of the equilibration vessel
P_D is the initial pressure (mm) of the deuterium
R is the gas constant (cm^3 mm [illegible] $^\circ$K^{-1})
T is the (ambient) temperature ($^\circ$K)
m is the weight of the metal (g)
C_{H_2} is the concentration of hydrogen (per cent) in the gas phase after equilibration
C_{D_2} is the concentration of deuterium (per cent) in the gas phase after equilibration
and $C^1_{H_2}$ is the initial hydrogen concentration (per cent) in the deuterium.

1.3 Equilibration Conditions

The usual method for determining suitable equilibration conditions is to heat pieces of metal of uniform hydrogen distribution for different times at different temperatures. This was considered rather tedious. The conditions used in this procedure were determined by observing the exchange with the aid of the mass spectrometer. This was accomplished by taking pieces of titanium metal (NBS No. 353) and heating them with the equilibration vessel open to the mass spectrometer through the leak. For each piece of metal the amplifier was set on masses 2, 3 and 4 respectively. The outputs were displayed on a strip chart recorder where temperature readings could also be plotted manually with time. A typical equilibration run is shown in Figure 2 which is a reproduction of the chart recordings. After a rapid initial rise in masses 2 and 3 during the first 10 minutes of heating, the gas phase reaches equilibrium in about 20 minutes. An equilibration time of 25 minutes was selected from observation of the mass 3 curve. The sharp decrease in mass 4 is due to both the solubility of deuterium in the metal with increasing temperature and the reaction $D_2 + H_2$ (from metal) $\rightleftharpoons$ 2HD.

These curves are subject to only a slight time lag due to diffusion between the hot zone of the equilibration vessel and the mass spectrometer source and are therefore a reasonably accurate representation of the equilibration kinetics with respect to time. Experiments using more rapid heating than that depicted in the figure have shown the time lag to be less than one minute.

2. RESULTS AND DISCUSSION

2.1 Mass Spectrometric Analysis

The isotopic analysis on the mass spectrometer is straight forward although the instrument itself needs to be equilibrated with deuterium. The frequency of this depends largely on the nature of other samples run on the machine. Relative sensitivities of H_2 and D_2 were measured and found to be the same (within one per cent) and the H_3^+ contribution to mass 3 was found negligible over the concentration range tested (gas phases containing > 50 per cent D_2). For samples with high hydrogen content (~ 2000 p.p.m.) it is necessary to reduce the sample weight, otherwise the gas pressure becomes too high for precise determination of H/D ratio. This increase in pressure is due to the evolution of hydrogen from the metal.

2.2 Determination of Blank

In the procedure adopted, a blank determination is carried out on the deuterium before each analysis. A true blank on the system would take into account possible exchange between the walls of the equilibration vessel during sample changes. This could be overcome by using a dry box for sample loading but this has not been done in this procedure as experience has shown that, provided sample changes are made quickly without exposing the inside of the vessel to the atmosphere for too long, any exchange that may take place has an insignificant effect on the results around the 30 p.p.m. level. The agreement obtained on standard samples validates this procedure.

2.3 Analysis of Titanium Metal Standards and Zircaloy-2

Using the conditions described, the NBS unalloyed titanium metal samples (Nos. 352-354) and Zircaloy-2 (No. 360a) were analysed by this procedure. The results are shown in Table 1. The agreement for the titanium samples is most satisfactory. Comparison of the results obtained by isotopic equilibration with those obtained by participants in the 'round robin' tests which led to the certification of the samples, (Sterling et al. 1962) shows how this technique measures up to other methods of gas analysis. Table 2 shows some statistical data for NBS No. 353 and compares the means and standard deviations for vacuum fusion, vacuum extraction and isotopic equilibration. The isotopic equilibration procedure yields generally higher reproducibility than vacuum extraction and is about the same as for vacuum fusion. The result obtained by the equilibration technique agrees very well with the population mean of the six laboratories and lies within the 95 per cent confidence limits (98.0 ± 3.7 p.p.m.).

Although the NBS Zircaloy-2 sample is not certified for hydrogen content, the result is considered valuable in the absence of any certified zirconium-base material. Since this sample is in a finely divided state, sampling errors due to inhomogeneities are minimised and therefore the material could be useful for interlaboratory comparisons. For this analysis, a platinum boat was used to contain the sample. Previous experience with finely divided Zircaloy has shown that when the sample is placed in contact with the hot walls of the silica tubes, fusion of the particles into the silica makes the tube unusable for further determinations.

SECTION B

ANALYSIS OF PREPARED SAMPLES OF KNOWN HYDROGEN CONTENT

1. PREPARATION

To obtain more data on the application of the procedure to zirconium and Zircaloy in particular, and also other metals of interest, attempts were made to prepare samples of known hydrogen content. Using the apparatus, hydrogen could be absorbed into pieces of metal by heating them in hydrogen. Determining the hydrogen content by weight difference was not successful owing to the need to use large pieces of metal (~ 1 g) to obtain sufficient accuracy in the weight measurement. It was also difficult to control the hydrogen uptake in the metal and the absorbed gas was found to be not uniformly distributed throughout the sample. This prevented sectioning of the sample into smaller pieces to reduce the gas pressure in the subsequent analysis.

The addition of hydrogen was achieved with suitable accuracy using the mass spectrometer to determine hydrogen partial pressures. In this way it was possible to find the amount of gas absorbed from measurements of the initial and final partial pressures. The initial partial pressure was determined by deriving a relationship between the mass 2 output for the equilibration vessel and the volume of the apparatus contained in the gas line bounded by the valves V1, V2, V3 and V4 and the mercury doser (see Figure 1).

The procedure involved placing a weighed piece of metal (0.2 - 0.3 g) in the tube and admitting hydrogen to the system at the set mercury doser pressure (16.5 mm). Valve V1 was then closed, the remaining hydrogen transferred to the two litre reservoir and the amplifier reading for mass 2 taken, making allowance for the instrument background. The sample was then heated to 700°C for 5 minutes and subsequently cooled. The gas phase was then admitted to the reservoir and the amplifier reading for mass 2 once again taken. From these two measurements the percentage of hydrogen absorbed was determined, using volume data obtained from prior calibration measurements. Using the gas law equation $PV = WRT$ the weight of hydrogen absorbed was calculated and thence the average hydrogen concentration in the metal. For each metal sample prepared in this way a blank was run to determine the residual hydrogen before addition.

2. RESULTS ON PREPARED SAMPLES

The samples of known hydrogen content were analysed by the procedure of Part A (Section 1.2) and the results compared (see Table 3). For zirconium, the procedure was tested over a fairly wide concentration range to check whether there was any bias towards higher concentrations. No bias was observed, indicating that the conditions chosen (V and P_D) were satisfactory for such variations in concentration.

Considering the errors involved in the addition of hydrogen and in the subsequent determination, the percentage recoveries lie within the overall experimental error and there is no significant bias.

Of particular interest is the result obtained for the NBS Zircaloy-2 which had previously been found to contain 18.5 p.p.m. The result obtained after addition justifies the confidence placed in this earlier result.

SUMMARY

The isotopic equilibration technique using the apparatus and procedure described is reasonably fast, simple to operate, and precise. The results obtained for certified samples and prepared samples demonstrate its application to a range of metals and alloys. The apparatus could be modified to accommodate more equilibration vessels to reduce sample processing time.

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TABLE 1

HYDROGEN RESULTS ON N.B.S. UNALLOYED TITANIUM METAL STANDARDS AND ZIRCALOY-2 BY THE ISOTOPIC-EQUILIBRATION MASS SPECTROMETRY PROCEDURE

Sample No.	Mean (p.p.m.)	Relative Standard* Deviation (per cent)	No. of Determinations	Certified Value (p.p.m.)
352	32.9	3.3	9	32 ± 2
353	98.5	2.3	14	98 ± 5
354	213.5	0.8	12	215 ± 6
360a (Zr-2)	18.5	2.2	7	-

* Relative Standard Deviation $= \frac{\sigma}{\bar{x}} \cdot 100$

TABLE 2

COMPARISON OF STATISTICAL DATA FOR THE ANALYSIS OF TITANIUM METAL STANDARD NBS NO. 353 (98 ± 5 ppm H_2) BY VACUUM EXTRACTION, VACUUM FUSION AND ISOTOPIC EQUILIBRATION METHODS

Laboratory	Method	Total No. of Determinations	Mean (p.p.m.)	Standard Deviation (p.p.m.)	Relative Standard Deviation per cent
No. 1	Vacuum Extraction	6	96.4	2.7	2.8
No. 2	Vacuum Extraction	14	100.3	8.1	8.1
No. 3	Vacuum Extraction	5	93.8	5.2	5.5
No. 4	Vacuum Fusion	6	103.0	1.7	1.7
No. 5	Vacuum Extraction	15	99.7	3.4	3.4
No. 6	Vacuum Extraction	107	95.0	3.1	3.3
A.A.E.C.	Isotopic Equilibration	14	98.5	2.0	2.3

TABLE 3

COMPARISON OF RESULTS OBTAINED ON VARIOUS METALS CONTAINING KNOWN AMOUNTS OF HYDROGEN BY THE ISOTOPIC-EQUILIBRATION PROCEDURE

Metal	p.p.m. Hydrogen Added (Including Blank)	p.p.m. Hydrogen Found	Per cent Recovery
Zirconium (Crystal Bar)			
No. 1	85	83	95.4
2	127	123	96.9
3	159	153	96.2
4	264	270	102.3
5	276	270	97.8
6	334	327	98.0
7	652	622	95.4
8	845	835	98.8
Zircaloy-2 (NBS 360a)	272	270	99.3
Niobium	106	105	99.1
Vanadium	192	196	102.1
Hafnium	1120	1110	99.1
Overall	4432	4364	98.46

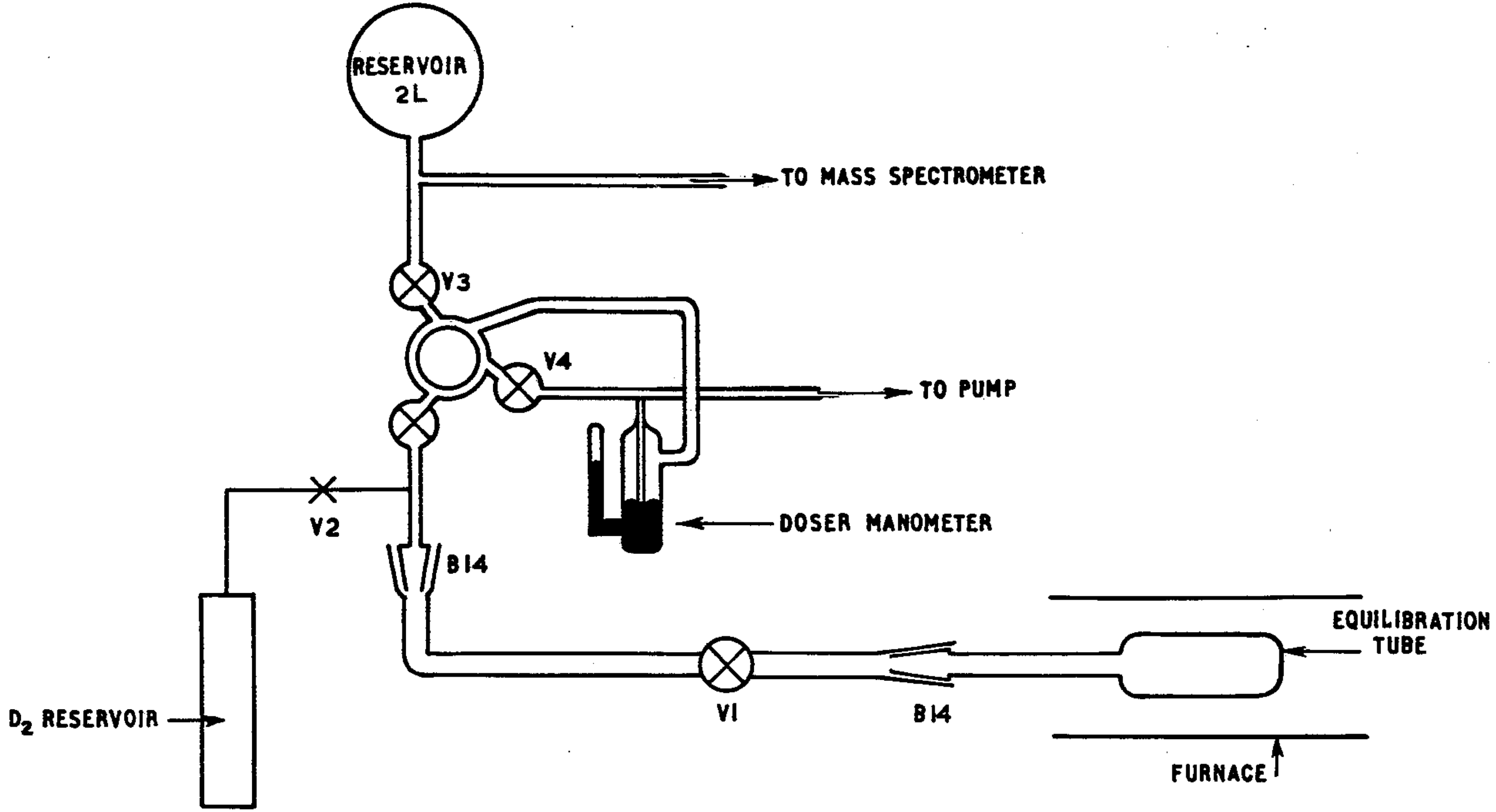

FIGURE 1. SCHEMATIC DIAGRAM OF EQUILIBRATION APPARATUS AND MASS SPECTROMETER GAS HANDLING SYSTEM FOR THE DETERMINATION OF HYDROGEN IN METALS BY THE ISOTOPIC-EQUILIBRATION PROCEDURE

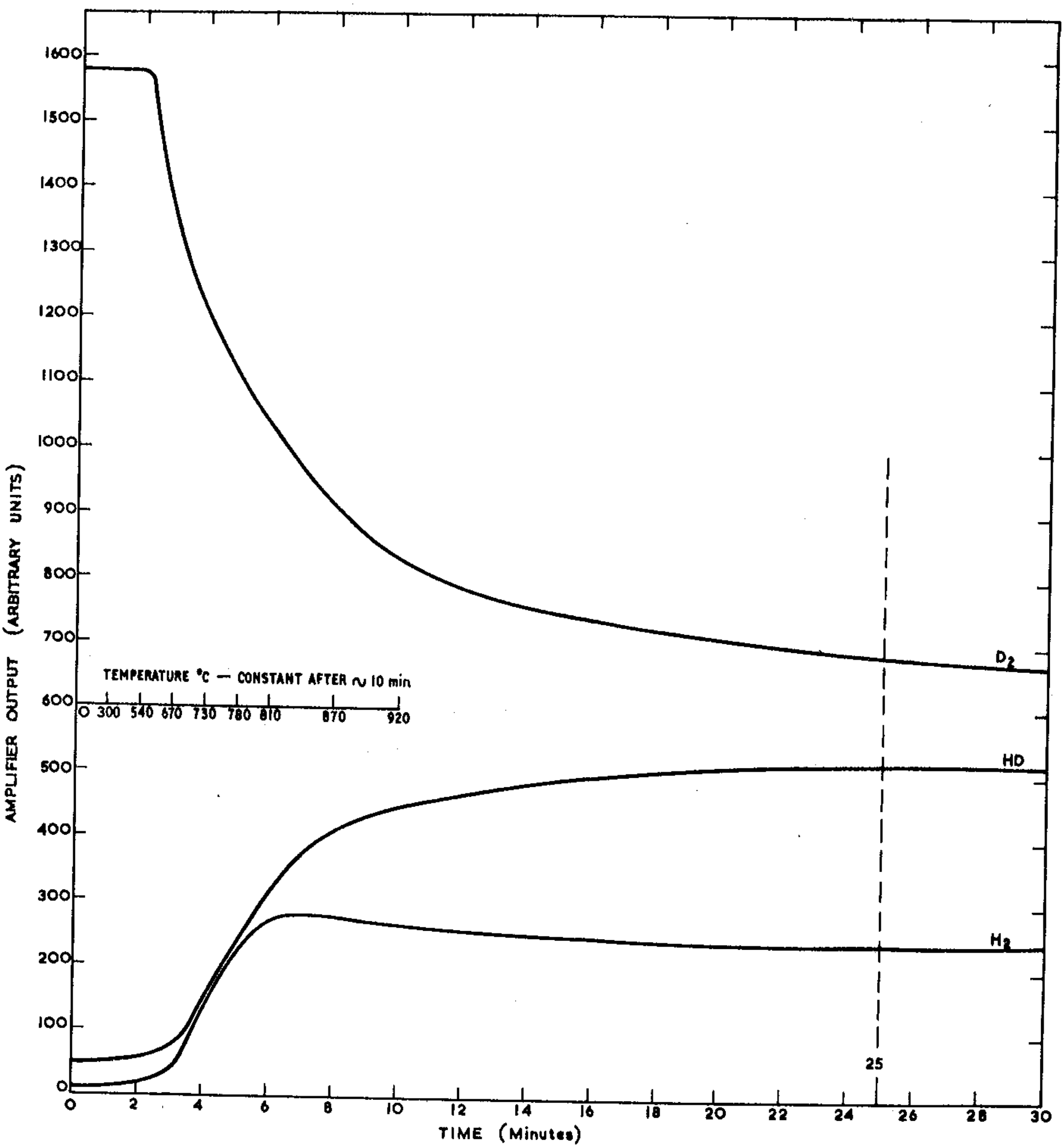

FIGURE 2. MASS SPECTROMETER AMPLIFIER OUTPUTS FOR MASSES 2, 3 AND 4 AS A FUNCTION OF HEATING TIME AND TEMPERATURE - DETERMINATION OF EQUILIBRATION CONDITIONS