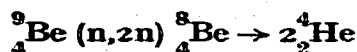# DETERMINATION OF NEUTRON-PRODUCED GASES IN BERYLLIUM BY GAS CHROMATOGRAPHY

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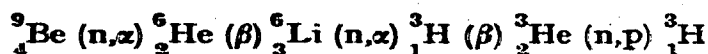
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INTRODUCTION

The low atomic weight of beryllium and its small cross section for thermal neutrons has led to considerable interest in this material and its oxide as moderators for fast neutrons in nuclear reactors. However, beryllium has an appreciable cross section for the following reactions with fast neutrons:

$$^9_4Be\ (n,2n)\ ^8_4Be \rightarrow 2\,^4_2He$$

and:

$$^9_4Be\ (n,\alpha)\ ^6_2He\ (\beta)\ ^6_3Li\ (n,\alpha)\ ^3_1H\ (\beta)\ ^3_2He\ (n,p)\ ^3_1H$$

Since the final products are gases, which can under certain circumstances concentrate as bubbles at grain boundaries, some concern has been felt that the physical properties of the moderator may be adversely affected as these reactions proceed[1-4]. A method is therefore required for determining isotopes of helium and hydrogen in beryllium-containing materials after various periods and conditions of irradiation.

ELLS[5] showed that helium and hydrogen may be quantitatively removed from beryllium by heating the metal under vacuum. The gases are rapidly removed if the beryllium is melted and this method has been adopted at the A.A.E.C. Research Establishment. Several methods of analysing the extracted gases have been compared.

EXPERIMENTAL

The vacuum extraction apparatus is shown in Fig. 1. Samples of beryllium weighing about 0.3 g are loaded into the system in such a manner that they can be dropped by means of a magnetically operated release mechanism into a silica crucible. Samples are melted by means of a radio frequency heater at approximately 1300°. The evolved gases are pumped rapidly from the furnace by means of a mercury diffusion pump. The gas is then Toepler pumped into a calibrated volume and the pressure measured. Fractions of the collected gas are set aside for analysis by mass spectrometry and gas chromatography and a fraction for the determination of tritium by gas counting.

(a) Tritium counting

Tritium is counted with a coaxial type counting tube in the proportional region using 10 % methane in argon at a counting gas pressure of 10 cm of mercury. These tubes
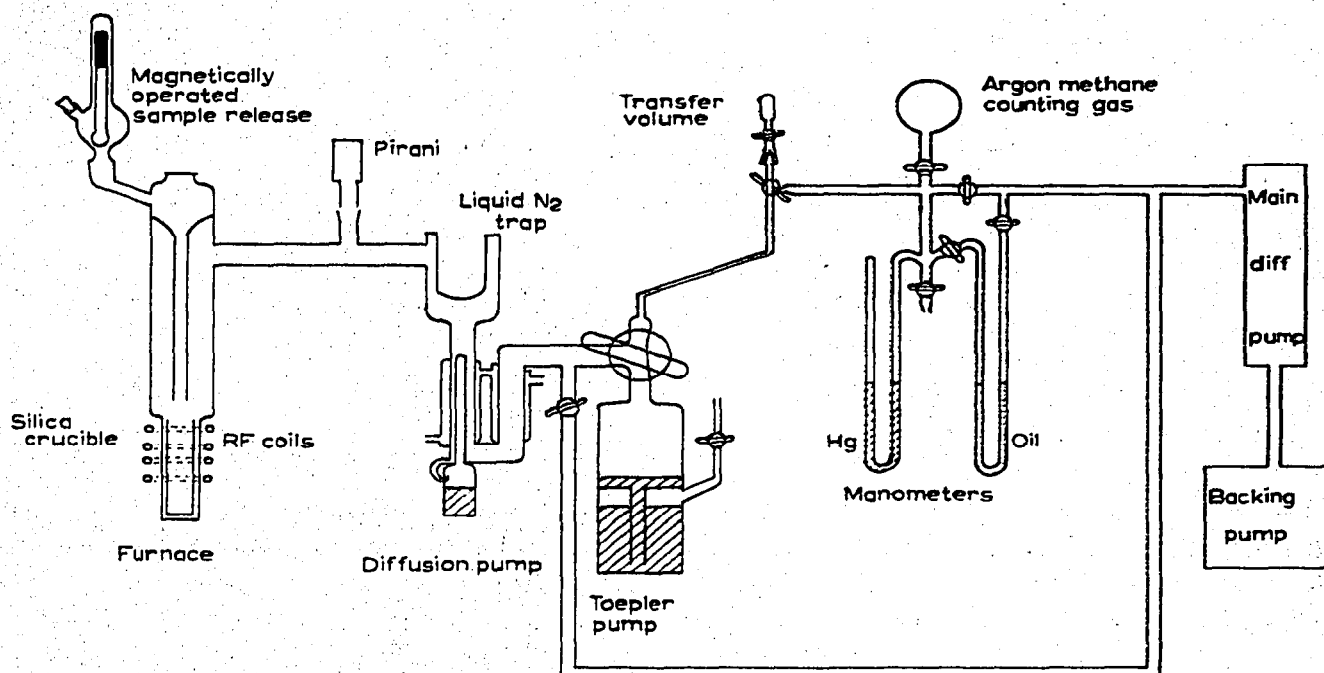
Fig. 1. Vacuum extraction apparatus.

have previously been calibrated against a pair of stainless steel compensating tubes. Owing to the high specific activity of tritium, gas dilutions of 10^4–10^6 times are required to obtain suitably low count rates.

(b) *Mass spectrometry*

A Metropolitan Vickers MS3 gas mass spectrometer is used for this purpose. In the lower mass range, the main contributors to various mass peaks are as given in Table I. The origin of deuterium is not known but by lowering the ionization voltage to about 20 V (when helium does not ionize) it has been shown that the mass 3 peak is very largely due to HD$^+$ and not ^{3}He$^+$. This is to be expected in samples which have

TABLE I

Mass No.	Species
1	H$^+$
2	H$_2^+$
3	HD$^+$ ^{3}He$^+$ (H$_3^+$)
4	HT$^+$ ^{4}He$^+$ (D$_2^+$)
5	Nil
6	T$_2^+$

recently been removed from the reactor since ^{3}He has a very large cross section for thermal neutrons and is burnt up as rapidly as it is produced. Changing the ionization voltage also permits HT$^+$ to be distinguished from ^{4}He$^+$. The large quantities of protium probably result from moisture present during processes of metal fabrication although a little is produced by the n,p reaction of ^{3}He.

(c) *Gas chromatography*

Molecular sieves were first used for the separation of the permanent gases by KYRYACOS AND BOORD[6] in 1957. This was followed by the work of TIMMS et al.[7] for the separation of impurities in carbon dioxide. The separation of hydrogen and helium has been reported by TOTH AND GRAF[8] and JANAK et al.[9,10] who first used palladium uniformly distributed on celite and later molecular sieves. More recently, MEYER et al.[11] reported the use of molecular sieves for the analysis of neutron-produced gases extracted from beryllium oxide.

The operating conditions for results reported in this paper were:

Detector. Perkin Elmer thermistor type maintained at 45°.

Column. Coiled stainless steel 7 ft. 6 in. long, 22 gauge, 1/4 in. O.D. packed with Linde 5 A molecular sieve —30 to + 44 mesh B.S.S.

Column temperature o°.

Carrier gas. Argon; flow rate of 65 c.c./min controlled by Negretti and Zambra precision pressure regulator.

Sampling system. Perkin Elmer gas sampling valve connected in line to a vacuum system and both oil and mercury manometers.

Column preparation. The molecular sieves were crushed and sieved to obtain the —30 to +44 fraction. The crushed sieves were then dried by heating in an oven at 400° for 3 h. The column was packed and then coiled at a red heat. Regeneration of the column was necessary initially and at intervals of about 3 months. This was accomplished by heating to 350° in a stream of argon.

Calibration. The column was calibrated by injecting standard mixtures of hydrogen in argon and helium in argon at various pressures.

A graph of peak height against volume of hydrogen or helium was linear up to 25 μl of both gases. Full scale deflection of the 1 mV recorder at maximum sensitivity corresponded to 2 μl of hydrogen and 2.5 μl of helium.

The uncorrected retention volumes for helium and hydrogen, at a carrier gas flow of 65 c.c./min. were 54.2 c.c. and 71.5 c.c. respectively.

Resolving power. At equimolar concentrations and so long as the quantity of either hydrogen or helium does not exceed 25 μl (*i.e.* column is not overloaded), the hydrogen is completely separated from helium. With concentrations of hydrogen larger than 25 μl, the hydrogen peak becomes asymmetrical with a sharp tail and a sloping front which overlaps the helium peak. Thus, helium in hydrogen may be detected down to approximately 0.1 % v/v, while in the reverse case (*i.e.* small concentrations of hydrogen in helium), no overlapping occurs and hydrogen may be detected down to 40 p.p.m. in 0.25 c.c. samples of helium.

RESULTS

Table II gives a comparison of results obtained by gas chromatography and mass spectrometry on samples taken from the helium gas blanket above the reactor HIFAR. The analyses were for total hydrogen ($H_2 + D_2 + T_2$) formed by radiolysis of the moderator.

A similar comparison showing results for total hydrogen and total helium extracted from several irradiated beryllium samples is shown in Table III.

The coefficient of variation of all the results is about 10 %. By the use of larger

TABLE II

ANALYSIS OF HELIUM GAS BLANKET ABOVE THE REACTOR HIFAR FOR HYDROGEN (p.p.m., v/v)

Sample No.	Gas chromatography	Mass spectrometry
I	200	180
2	500	580
3	200	190

TABLE III

COMPARISON OF THE COMPOSITION OF GAS FROM IRRADIATED BERYLLIUM BY GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

Sample No.	Gas chromatography		Mass spectrometry	
	H_2%	He%	H_2%	He%
I	64.5	31.1	64.4	32.6
2	51.4	48.6	48.3	49.0
3	73.5	23.5	70.4	23.0
4	54.3	45.7	51.0	45.3
5	83.3	10.4	83.7	10.7

TABLE IV

ANALYSIS OF RADIOGENIC GASES FROM BERYLLIUM METAL

	Sample No. 1			Sample No. 2		
Volume gas extracted per g of beryllium (c.c.)	0.609			0.432		
	Mass spectr. (%)	Gas chrom. (%)	Counting (%)	Mass spectr. (%)	Gas chrom. (%)	Counting (%)
H_2	64.0		—	48.0		—
D_2	0.02	64.5	—	Not detected	51.4	—
T_2	0.3		0.67	0.3		0.71
^3He	Not detected	31.1	—	Not detected	48.6	—
^4He	32.6		—	49.0		—
(CO + N_2)	0.9	—	—	0.73	—	—
O_2	0.1	—	—	0.1	—	—
A	1.4	—	—	0.3	—	—
CH_4	0.3	—	—	1.5	—	—
CO_2	0.1	—	—	0.1	—	—

samples even smaller concentrations of hydrogen could be detected by gas chromatography.

The chief source of error in the results obtained by gas chromatography, is in the measurement of the sample pressure. The gas sampling valve has a measureable leak rate at sample pressures in the region of 1 cm of mercury which are used and this involves a small correction.

Table IV is the complete gas analysis of two typical samples by all three methods.

The quantity of tritium is usually too low to be determined with any precision by the mass spectrometer.

Protium, methane and carbon monoxide originate from impurities present in the metal before irradiation.

DISCUSSION

These preliminary results show that gas chromatography is a feasible method for determining hydrogen and helium extracted from irradiated beryllium-containing materials. In the near future we shall try to separate isotopes of hydrogen on columns maintained at low temperatures as described by several previous workers[12-14]. This will help to confirm the presence of the deuterium observed by the mass spectrometer since it is interesting to decide whether this is produced during irradiation or arises from contamination from the reactor moderator.

The gas chromatographic results can be obtained more cheaply and rapidly than those using the mass spectrometer and are less liable to error. When using gas chromatography alone, the entire sample can be diluted with argon to a pressure which makes the effect of the sampling valve leak negligible. An ionisation detector in the column exit in addition to the thermistor detector should also allow an independent gas chromatographic estimation of tritium in the same sample.

SUMMARY

Gases present in beryllium after neutron irradiation have been extracted by vacuum melting. The helium and hydrogen content of the extracted gas has been determined by gas chromatography and the results compared with those obtained by mass spectrometry.

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