DETECTION OF VOLUME PARTS PER MILLION OF PERMANENT GASES IN HELIUM

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I. INTRODUCTION

In high temperature helium cooled graphite moderated nuclear reactors the partial pressures of chemically reactive gases (such as H_2, O_2, N_2, CO, CO_2 and CH_4) must be reduced to the order of 10^{-6} atm in order to limit chemical reaction with the moderator graphite[7]. It is therefore necessary to carry out analyses for these partial pressures in the coolant (up to total pressures of 25 atm) involving the determination of volume parts per million (v.p.m.) of the reactive gases in helium.

Gas chromatography with its advantage of rapid analysis of one sample for several gases is one of the possible analytical methods favoured. Since the object is to measure v.p.m. of other gases in samples consisting almost entirely of helium, the obvious carrier gas to use through the separation column and detector is helium itself. This eliminates the dominant helium peak which would occur on the chromatogram with any other carrier gas and which would be difficult to resolve in the column from peaks for v.p.m. amounts of other permanent gases in the sample. Separation of permanent gases at comparable low partial pressures can easily be achieved in molecular sieve and silica gel columns. The separation of gases in a sample must, however, be obtained without excessive decay of their initially low partial pressures occurring in the column due to axial diffusion or mixing and resistance to adsorption on the packing, otherwise the detection would be made more difficult. The volume of the sample, the adsorbent, the temperature and dimensions of the column and the flow rate of the carrier stream must therefore be chosen carefully to minimize this decay.

The most promising method of detection of v.p.m. of permanent gases in helium after chromatographic separation appears to be radioactive ionization. The principle of this method, as originally used by LOVELOCK[1] to detect v.p.m. of organics in argon, is that radiation from an active source (such as ^{90}Sr) placed in an ionization cell is absorbed by argon flowing through the cell to raise some atoms to a metastable energy level of 11.6 eV. These atoms collide and ionize atoms or molecules of other gases present having ionization potentials less than 11.6 eV. Electrodes in the cell at a suitable voltage difference collect the ions formed to give an ionization current dependent on the amounts of other gases in the argon. By careful arrangement of the cell geometry the increase in ionization current produced by even low v.p.m. of other gases is made comparable with the standing current for pure argon. The high sensitivity and accuracy of this method is due to this effect and to the stability of radioactive ionization in comparison with other means of ionization (such as flames).

With a metastable energy of 11.6 eV, argon is not capable of directly ionizing permanent gases all of which have ionization potentials greater than 12 eV (see Table I). Helium, however, has a metastable energy of 19.8 eV which is higher than the ionization potentials of all permanent gases except neon and should therefore be capable of ionizing these gases. BERRY[2], SERPINET[3] and KARMEN et al.[4] have shown that the Lovelock type of ionization cell can detect n.t.p. milli-micro litre quantities of permanent gases introduced in small volumes into a helium carrier stream. Data are lacking, however, on the sensitivity of the detector to low v.p.m. of permanent gases in helium. This detector with a helium carrier stream is therefore an obvious choice for use in chromatographic analysis of v.p.m. of permanent gases in helium providing it has the necessary sensitivity.

TABLE I

IONIZATION POTENTIALS

Gas	Ionization potential (eV)
He	24.5
Ne	21.5
A	15.7
CH_4	14.5
N_2	14.5
Kr	13.9
O_2	13.5
H_2	13.5
Xe	12.1

In using the detector to indicate the partial pressure of a chromatographically separated pulse of another gas in the carrier gas, the chromatographic peak observed shows an increase in ionization current above the standing value for the carrier gas as the pulse passes through the detector. This increase is not necessarily a measure of the absolute partial pressure of the pulse but only of the difference between this partial pressure and the partial pressure of any of this gas remaining in the carrier gas when noting the standing current. The observed value of the partial pressure of the pulse is in error on the small side by this latter amount. If this error is to be comparatively small the carrier gas must be so pure that the partial pressures in it of all gases, for which analysis is being made, are small compared with the values being analysed.

This paper describes an experimental programme to determine the accuracy of the Lovelock radioactive ionization cell for the detection of v.p.m. of permanent gases in a chromatographic carrier stream of purified helium. A purifier was built to reduce as low as possible the concentration of all other gases in a helium stream from commercial high pressure cylinders. Measurements were made of the purity of the helium stream and of the detector stability and sensitivity to various gases added to the purified helium stream.

2. EXPERIMENTAL

Commercial helium from high pressure cylinders usually contains up to 10 v.p.m. of various permanent gases and considerably greater amounts of water vapour. Before

using this helium as a carrier stream for chromatographic analysis for v.p.m. of permanent gases it is therefore necessary to purify it. The most powerful means of helium purification is a liquid helium-cooled (4°K) trap to freeze out all other gases and vapours to very low levels. This, however, is inconvenient for routine use. Other methods of purification are reviewed by ANTILL et al.[5]. BERRY[2] has combined both chemical and adsorption trapping to produce a purifier which was thought to reduce most impurities to levels comparable with or less than the limits of detection of the Lovelock detector. A similar purifier was accordingly built for the present work.

The experimental programme was divided into two main parts, investigation of the detector stability and sensitivity and investigation of the purity of the helium stream.

The detector stability and sensitivity depend respectively on the variations in ionization current

    (i)   occurring at random from time to time for the purified carrier stream and

    (ii) produced by additions of other gases to the carrier stream.

The former can easily be studied by recording the detector standing current. Investigation of the latter requires a means of producing known v.p.m. ratios of other gases in helium. For this purpose a flowmeter mixing train was built with which it was possible to add flows of other gases to the helium carrier stream to give ratios down to $1:10^8$. The use of this train enabled a study to be made of the sensitivity of the detector to various gases. By reducing the amounts of gases added until a limit was reached at which the increase in ionization current became comparable with the random variation in the standing current the minimum significantly detectable ratios were determined.

To establish that any gases remaining in the purified stream were present only at levels comparable with or less than the limits of detection presented a problem as there was no direct method of measuring them. This difficulty was dealt with in two ways, both using a liquid helium cooled trap which had been proved to have a high trapping efficiency in the v.p.m. range for all permanent gases. Firstly, it was shown that passing the purified helium stream through this trap immediately before the detector produced no significant fall in ionization current below its value when not using the trap. Therefore, since the trap efficiency was high any gases which it removed could have been present only up to v.p.m. comparable with the detectable limits. Secondly, a large measured volume of the helium was passed through the trap, and the trap was then isolated and warmed to room temperature. The solidified gases were thereby evaporated back into the closed trap and their partial pressures were amplified by a known ratio to measurable values. The contents of the trap were then analysed by both chromatography and mass spectrometry. From the results of these analyses the original partial pressures of all other gases in the purified helium stream were calculated.

3. APPARATUS

The experimental equipment consisted of a metal purification train supplying purified helium to three pieces of all-glass apparatus. These were:

    (i) The liquid helium trap for determination of the purity of the purified helium.

    (ii) The flowmeter mixing train for calibration of the ionization detector for v.p.m. additions of other gases to the purified helium.

(iii) The gas sampling valves and separation column for chromatographic analysis of samples of gas mixtures.

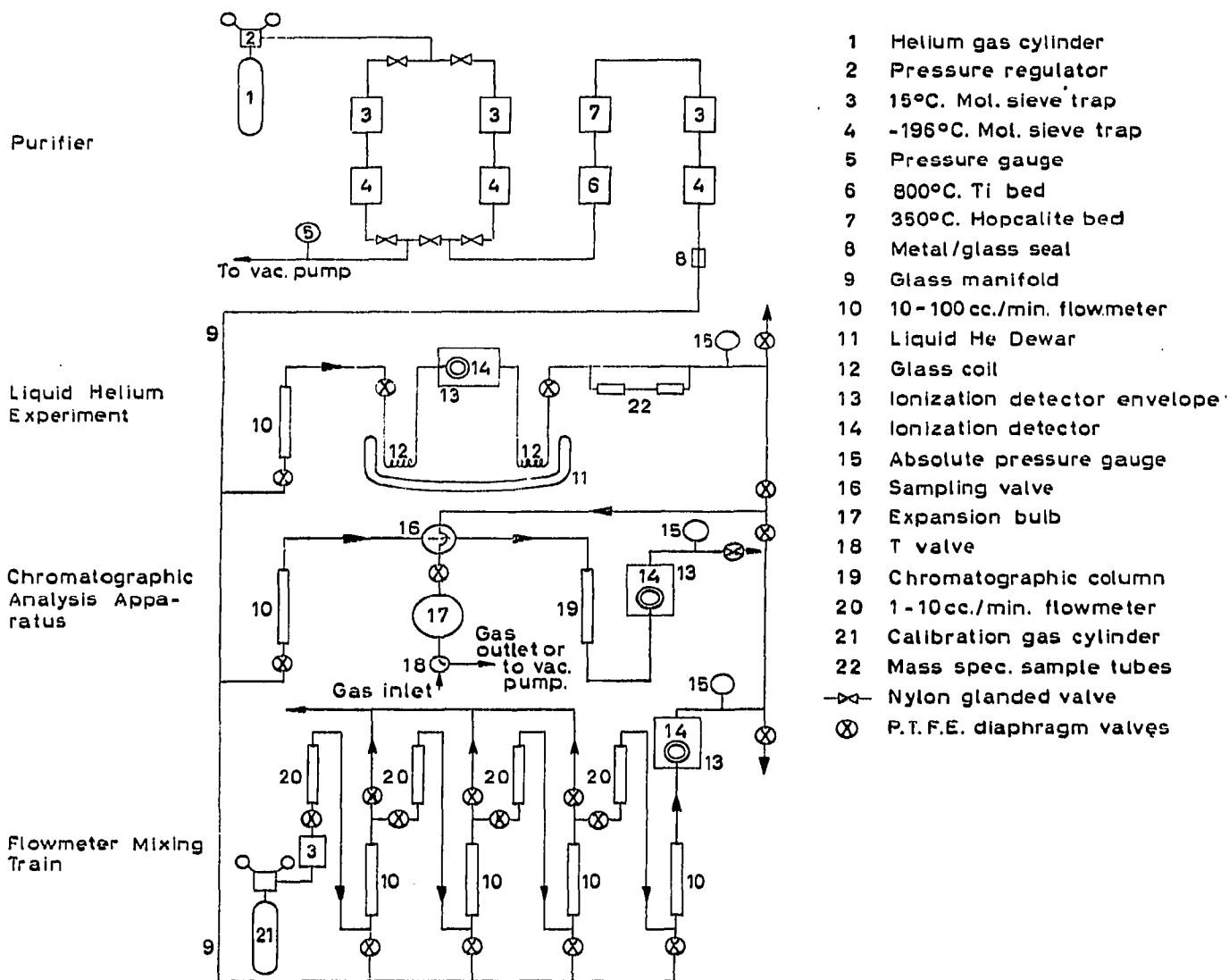The layout of these experiments is show diagrammatically in Fig. 1.

1	Helium gas cylinder
2	Pressure regulator
3	15°C. Mol. sieve trap
4	-196°C. Mol. sieve trap
5	Pressure gauge
6	800°C. Ti bed
7	350°C. Hopcalite bed
8	Metal/glass seal
9	Glass manifold
10	10-100 cc./min. flowmeter
11	Liquid He Dewar
12	Glass coil
13	Ionization detector envelope
14	Ionization detector
15	Absolute pressure gauge
16	Sampling valve
17	Expansion bulb
18	T valve
19	Chromatographic column
20	1-10 cc./min. flowmeter
21	Calibration gas cylinder
22	Mass spec. sample tubes
—▷◁—	Nylon glanded valve
⊗	P.T.F.E. diaphragm valves

Fig. 1. Flow sheet: purifier and experimental equipment.

3.1 Purification train

The purification train, similar to that used by BERRY[2], was supplied with commercial helium from high pressure cylinders. The helium passed through the following four stages, in series (Fig. 1):

(i) Room temperature (3) and liquid nitrogen (4) cooled molecular sieve traps removed the bulk of the H_2O, CO_2 and easily condensable gases. The sieve was Linde grade 5A, $1/16$-in. pellets.

(ii) Titanium chips (6) at 800° removed N_2.

(iii) Hopcalite (7), a mixture of copper and manganese and their oxides, trapped O_2 as CuO and oxidized the H_2 to H_2O and the CO to CO_2.

(iv) Final room temperature and liquid nitrogen-cooled molecular sieve traps removed the H_2O and CO_2 formed in the previous stage.

All these six traps were 6-in. long cylinders of i.d. *ca.* 2-in. Pyrotenax heating cable was wound round the cylinders to heat them when required. The first stage molecular sieve traps, which removed the bulk of the impurities, were duplicated in parallel to allow regeneration by heating without interrupting the flow. To improve heat transfer, a $1/_8$-in. d. coiled pipe was tried out initially for the liquid nitrogen sieve trap, but owing to its tendency to become blocked by ice plugs near the liquid nitrogen surface was discarded in favour of cylinders having $1/_2$ -in. d. inlet pipes.

All traps and piping in the train were of stainless steel and were washed with nitric acid and acetone before assembly. Nylon glanded valves (for flow control) and compression couplings were used upstream of the second stage. From this stage onwards there were no valves or couplings and an all-welded construction was used to ensure leak tightness.

The outlet from the purification train led through a metal to glass seal to a glass manifold (9 in Fig. 1) from which the purified helium flowed to the glass apparatus. Each apparatus was attached to this manifold by glass-blowing to form an integral all-glass construction. Most of the valves used had P.T.F.E. diaphragms. The only others were those for introducing gas samples into the carrier stream before the separation column; these, being multi-way valves, were necessarily greased cocks. The flow meters used were of the glass tube rotameter type with stainless steel floats. Pressures were measured by stainless steel diaphragm absolute pressure gauges reading from 0 to 1000 mm Hg with an accuracy of $1/_2$ mm Hg. The ionization detectors were at room temperature which in the controlled ventilation laboratory varied from 20° to 25°.

3.2 Gas sampling valve and separation columns

The apparatus for the chromatographic analysis consisted of a flowmeter to measure the carrier flow, a sample introduction valve, a separation column and an ionization detector. The sampling valve (16 in Fig. 1), was a grease cock with two pairs of diametrically opposite inlets and outlets to its body. Its barrel had two separate bores each connecting an inlet and an outlet. The carrier stream was passed through one bore and the stream to be sampled through the other. By rotating the barrel through 90°, gas from the sample stream was first trapped in its bore and then injected as a slug into the momentarily interrupted carrier flow. The column (19 in Fig. 1) was a 3 mm bore 35 cm long glass tube. It was packed with either 50–60 mesh silica gel or a molecular sieve depending on the gases to be separated. It was wrapped with heating tape which could warm it up to 200° for regeneration and operation above room temperature.

3.3 Liquid helium trap

The apparatus for the liquid helium experiment (Fig. 1) consisted of a flow-meter, a 1 mm bore 25 cm long coiled glass tube, an ionization detector and another similar coil. These coils were positioned in a liquid helium dewar which was itself surrounded by a liquid nitrogen dewar, and when cooled to the normal boiling point of liquid helium (4°K) acted as traps to freeze out other gases from the helium passing through them. The detector was placed outside the dewar with a sufficient length of tubing between

it and the liquid helium to ensure that the helium gas arriving at it had warmed from 4°K to room temperature. The second coil was used as a safeguard against back diffusion to the ionization detector from the outlet during filling with liquid helium when the contraction on cooling the gas in the coils temporarily stopped the flow. It was probably unnecessary because during filling the outlet valve was closed and the whole unit was leak tight to high vacuum standards. The outlet tube from the second coil had a parallel loop of mass spectrometry breaker seal sample tubes. When samples were required these tubes could be sealed off and removed. Further downstream the outlet flow passed through the chromatographic sampling valve (16 in Fig. 1) and finally to the atmosphere through a P.T.F.E. diaphragm valve.

In running this experiment the gas pressure and flow rate were controlled by adjustment of the P.T.F.E. valves at the beginning and end of the apparatus. The pressure was usually held at a few mm Hg above atmospheric pressure. This increase in pressure was sufficient to liquefy some of the helium gas flowing through the coils cooled by the liquid helium at its normal boiling point and made the flow erratic. To prevent this the liquid surface in the dewar was pressurised to a few cm Hg with helium. The resulting rise of about 0.1° of the liquid above its normal boiling point was then sufficient to avoid liquefying the gas in the coils.

3.4 Flow meter mixing train

For calibration experiments the flow meter mixing train was built to provide a stream of purified helium with which constant known flows of other gases could be mixed down to a ratio of $1:10^8$. It consisted of four streams of purified helium taken from the manifold though flowmeters (10 in Fig. 1) at rates up to 100 cc/min. Into the first of these streams, at a point before its flowmeter, a second gas from a cylinder and molecular sieve trap was metered through a smaller flowmeter (20 in Fig. 1) at rates down to 1 cc/min. (This is about the lowest gas flow accurately measurable by a rotameter.) The larger flowmeter both measured and mixed the two flows to give dilutions down to $1:100$. From this mixture 1 cc/min was metered into the second purified helium stream to give dilutions down to $1:10,000$ and so on. By using the four stages of the train it was possible to achieve dilutions down to $1:10^8$. This continuous flow method, in spite of the wastage of about three quarters of the purified helium to the atmosphere, was preferred to a batch mixing method of making up samples for two reasons. Firstly it provides a convenient and infinitely variable control of the dilution ratio. Secondly, because of the continuous flow, the amounts of gases adsorbed on the glass tube approach equilibrium with the gas phase, whereas in the batch mixing of large with small volumes of gas, there is always uncertainty as to how much the partial pressure of the dilute component may be altered by adsorption or desorption on the walls of the vessel.

The gas stream from the fourth mixing stage passed through an ionization detector and a P.T.F.E. diaphragm valve to the atmosphere. Using this apparatus it was possible to calibrate the ionization current of the detector against steady known v.p.m. additions of various gases to the purified helium stream.

A second outlet from the fourth stage of the mixing train led through the sample side of the chromatographic sampling valve. By rotating this valve through 90°, a sample of this stream was introduced into the carrier stream to the separation column. This enabled a direct calibration of either the chromatogram area or the peak height

to be made against samples of known v.p.m. addition. The calibration of peak height differed from the steady calibration because, as the sample passed through the column to the detector, the gas in it diffused forwards and backwards thus reducing its peak v.p.m.

A direct check that the mixing of the various gas streams in the flowmeter train was complete and that the calculated mixing ratios were accurate was considered desirable. This was done using the chromatographic analysis apparatus and the following device. A glass expansion bulb (17 in. Fig. 1) with two outlets was glass blown into the line from the sample side of the chromatographic sampling valve (16 in Fig. 1). The other outlet from the bulb led to one of the arms of a "T" valve (18 in Fig. 1) with a "half moon" bore through its barrel. The bulb was connected through one arm and the leg of the "T" valve to a vacuum pump. After evacuation the bulb was isolated under vacuum by rotating the barrel of the "T" valve clockwise to a position where it connected the leg and the other arm. A gas stream was then passed through its bore. Further clockwise rotation of the barrel isolated the bore filled with gas until it opened only to the bulb. The bore full of gas then expanded into the bulb and sample bore of the sampling valve (16 in Fig. 1). The volume ratio of the expansion was about 1:4,000. Hence if the gas stream had been passed at one atmosphere through the "T" valve, the sample bore of the sampling valve was filled with gas at a pressure of 250×10^{-6} atm. (This pressure could be increased in units of 250×10^{-6} atm by repeating the latter part of the above procedure.) By rotating the barrel of the sampling valve a sample of the gas at this pressure was introduced into the column carrier stream. The chromatogram thus obtained was compared with that obtained by sampling 250 v.p.m. of the same gas in helium at one atmosphere, prepared by the flowmeter train, since both samples of the same volume and temperature should be at the same partial pressure, and, provided the mixing train was operating accurately, should therefore contain the same mass.
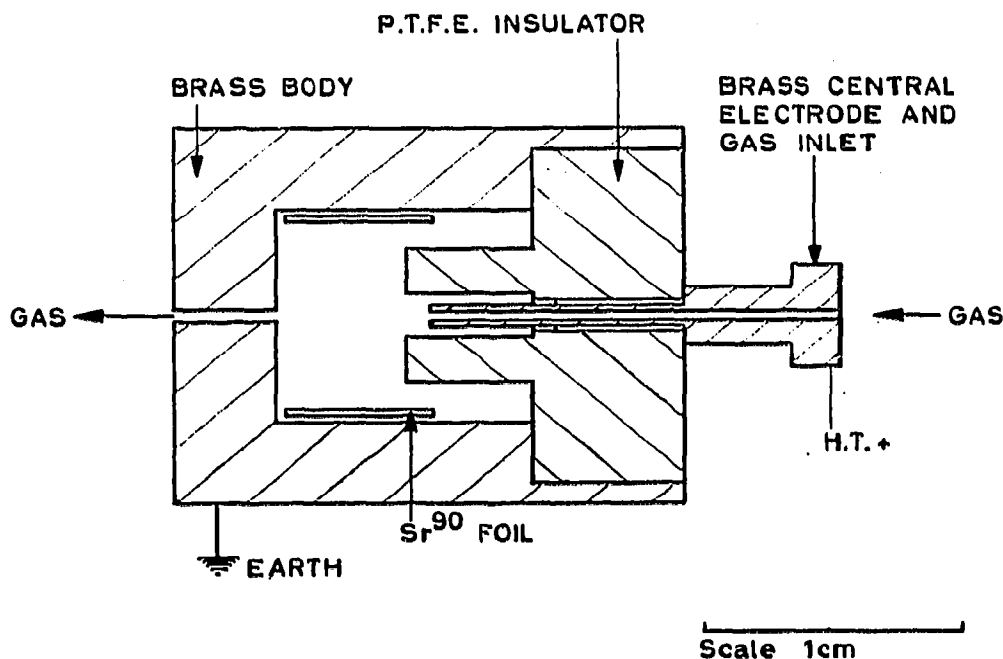

Fig. 2. Detector.

3.5 Detectors and electronics

The three ionization detectors used were commercial argon micro detectors of W. G. Pye Ltd., Cambridge. As supplied for use with small carrier flows from capillary columns each detector casing had a second inlet intended for the admission of a scavenge flow. This was not necessary in the present work with high carrier flows and the second inlets were blanked off. The detectors contained 10 mC ^{90}Sr radioactive sources. Their dimensions are shown in Fig. 2.

Because they were not leak tight to high vacuum standards they were totally enclosed in glass envelopes for the present work. The voltage applied to the detectors was obtained from a power pack which provided voltages of 750, 1000, 1250 and 1500 V. The current from the detector was amplified for recording by a Honeywell Brown 10 mV recorder. The amplifier had various ranges with which full scale deflection on the recorder could be obtained for currents in the range 1.4×10^{-9} to 4.7×10^{-7} amps. The amplifier also had several ranges of attenuation with which up to 95 % of the current could be backed off leaving only 5 % for amplification. This was useful for the analysis of the lowest v.p.m. which gave changes of current comparable with the standing value.

4. RESULTS

4.1 Commissioning experience

After the equipment described above had been built and satisfactorily pressure and vacuum tested the molecular sieve traps were regenerated to drive off adsorbed gases. Regeneration was carried out by holding the traps at 300° under vacuum for 12 h. After this period dew point measurements of a helium stream passed through the hot taps showed the H_2O vapour pressure to have fallen to 0.9 mm Hg. From Linde data[6] for H_2O adsorption on molecular sieves this indicates an H_2O weight loading of the sieve of 1 %. This weight loading at 15° has an H_2O vapour pressure in equilibrium with it of 5×10^{-5} mm Hg. Extrapolation of the data to —196° indicates a quite insignificant equilibrium vapour pressure.

The purification train was then put into service at 3–5 lb/in² g pressure of helium. During the commissioning period and first attempts of the analytical experiments several modifications to the pipe work layout were made to give the final form shown diagrammatically in Fig. 1. Experience gained during this period showed that when the purification train was started up after exposure to the atmosphere the outlet helium usually contained up to 1000 v.p.m. of impurities. This ratio then decreased over a period of hours to some 50–100 v.p.m. as the impurities diffused out of dead pockets in the pipe work. After this time the ratio continued to decrease but at a very much slower rate as impurities adsorbed on the pipe walls, desorbed into the helium stream. The rate of degassing the walls could be greatly increased by flaming the glass and metal pipes to red heat and heating the P.T.F.E. valves to 200°. Usually, after two to three days the standing current of the ionization detectors had fallen to a steady minimum value.

The purification train has been operated continuously with helium flows of between 100 and 500 cc/min. This experience shows that the first stage molecular sieve traps have sufficient capacity for up to a month's running without letting impurities break through. The fourth stage sieve has operated satisfactorily for up to

six months without regeneration. No trouble has been experienced with the titanium and hopcalite stages.

After the modifications and trials were complete the purification train was run without stop for three months with purified helium always flowing through all the glass ware. The experiments described below were carried out during this period.

4.2 Detector stability and sensitivity

The experimental programme began with an investigation of the effects of the variables which influenced the standing current of the detector for helium from the purification train. These variables were pressure, temperature, voltage and helium flow rate.
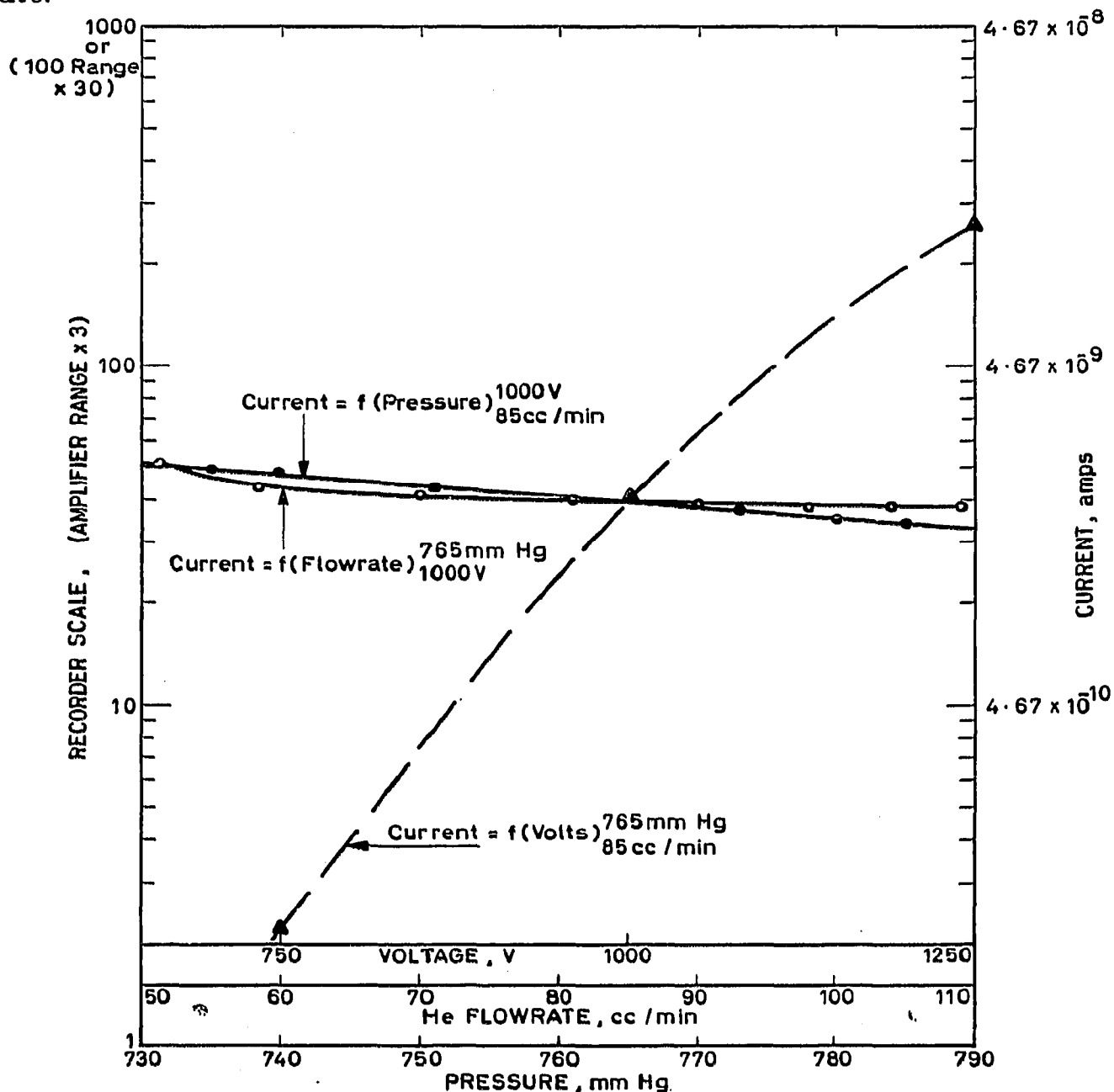

Fig. 3. Effects of pressure, voltage and helium flow rate on standing current.

The standing current was found to be approximately inversely proportional to pressure, in the range 730 to 800 mm Hg, doubling for a decrease of 90 mm Hg (Fig. 3). The effect of variation of temperature in the range 20 to 25° was such that provided the pressure was also varied to keep the helium density constant the standing current was unchanged. Increase in voltages up to 1250 V applied to the detector gave steady increases in standing current (Fig. 3). Higher voltages and even 1250 V at pressures below 750 mm Hg appeared to produce spark discharges with momentarily very high currents. Increasing the helium flow rate up to 60 cc/min slightly decreased the standing current, but from 60 cc/min up to at least 110 cc/min the standing current was independent of flow rate (Fig. 3).

From these results it was decided to select standard conditions for all further measurements. Pressure and temperature of 765 mm Hg and 23° were chosen as conveniently practical values. A voltage of 1000 V was chosen, as being the highest voltage which would give maximum sensitivity without causing spark discharge. A flow rate of 85 cc/min was chosen because of the insensitivity of the standing current to flow rates between 60 and 110 cc/min.
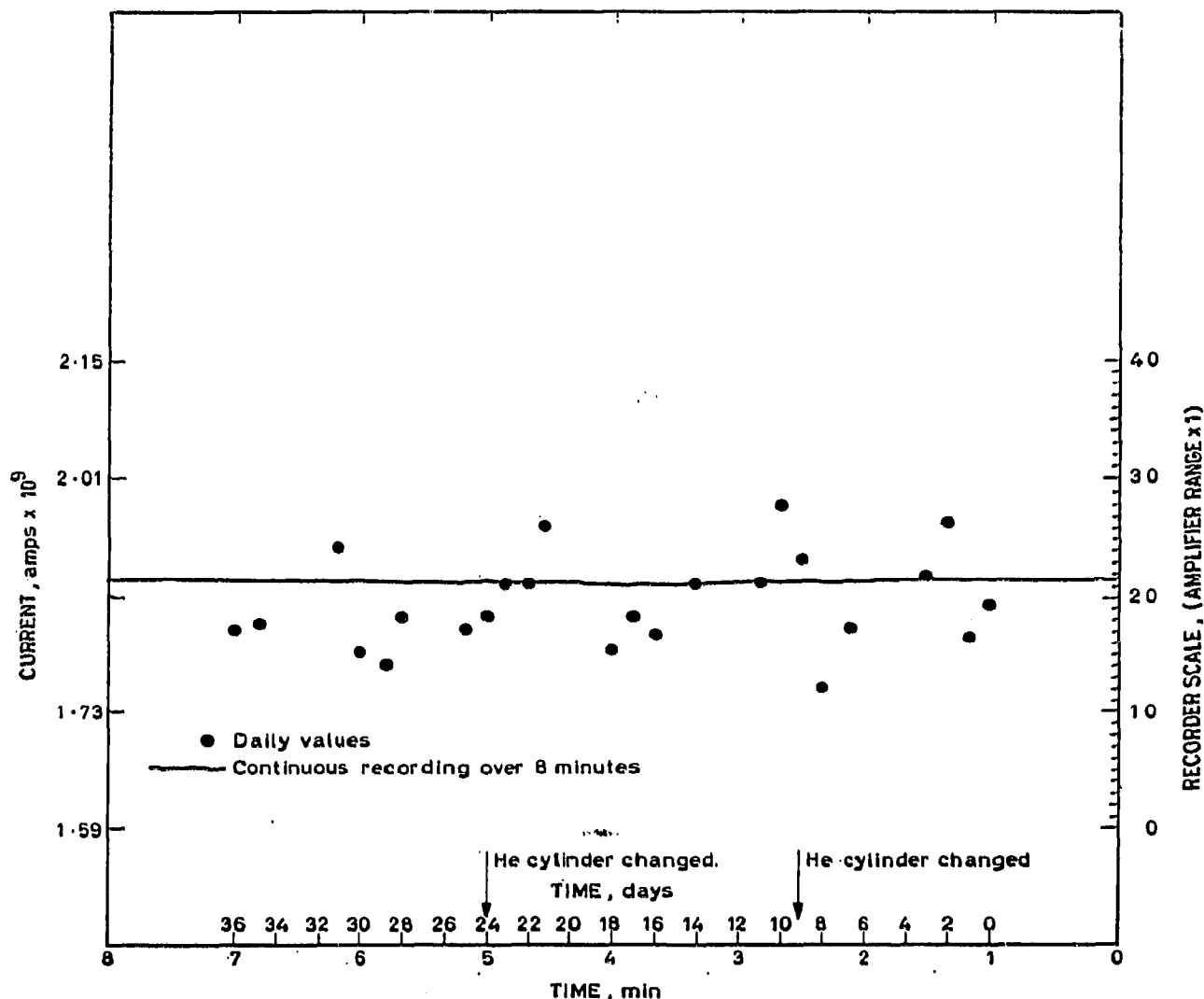
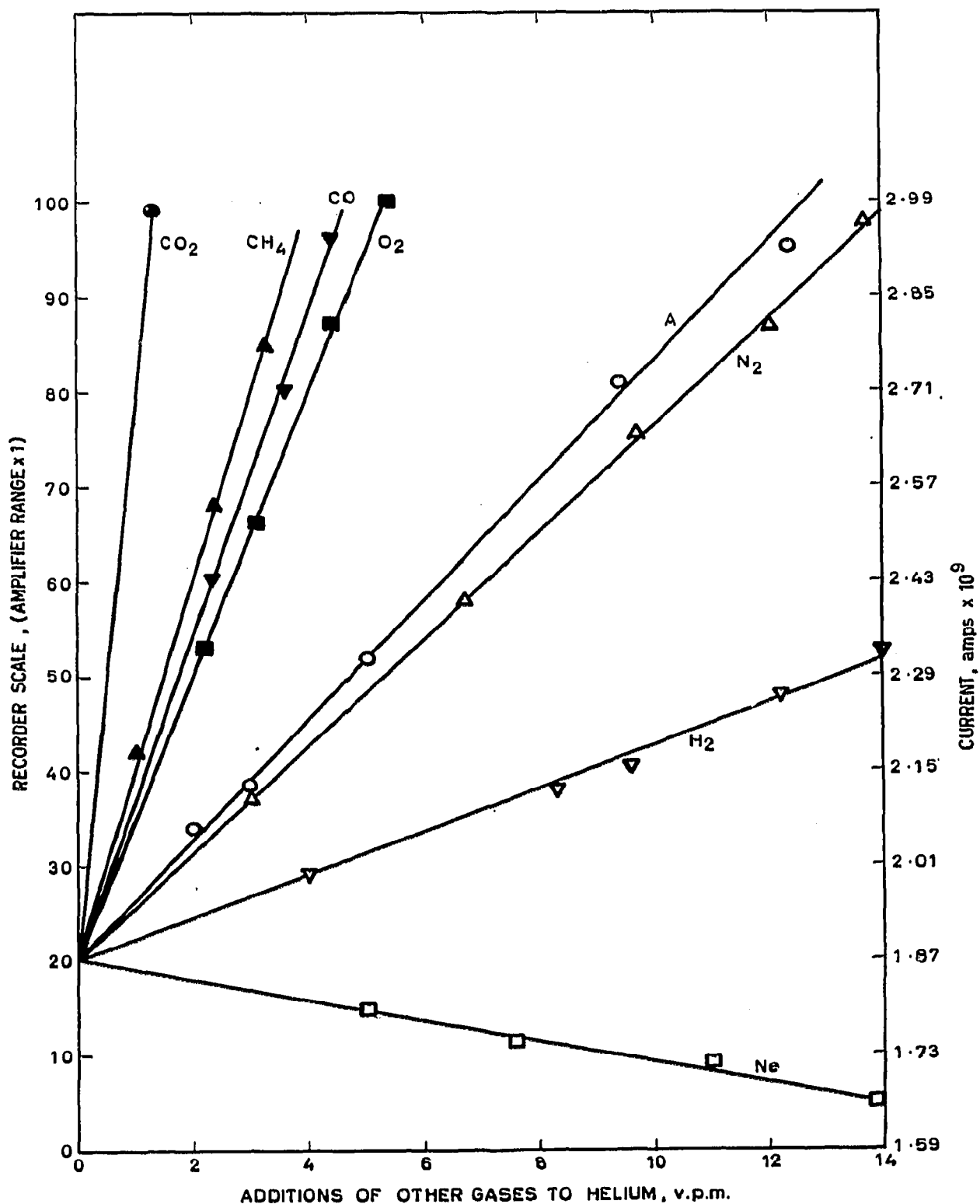Fig. 4. Stability of standing current at standard conditions.

Fig. 5. Calibrations of detector.

The stability of the standing current was investigated next under standard conditions. The maximum amplification available from the electronics was accordingly used with appropriate backing off so that one scale division on the recorder chart

was equivalent to a change in current of 1.4×10^{-11} amps. An example of the short term stability is shown by the continuous line (Fig. 4) drawn on the chart over an interval of 8 min. The random variations on this line are obviously sufficiently small to make a change of one scale division significant. The long term stability is shown by the point values (Fig. 4) plotted daily over the 36 days during which these experiments were carried out. The variation of the points may have been due either to variations in the purity of the helium from the purification train or to inaccuracies in setting the standard conditions.

Calibrations of the detector sensitivity to various gases were made using the flow meter train to mix constant known v.p.m. additions of other gases with the purified helium stream. Increases in ionization current are plotted against v.p.m. additions (Fig. 5). The results show that the sensitivity is linear over the ranges plotted and varies with different gases, decreasing in the order CO_2, CO, O_2, A, N_2, H_2, Ne. Ne was exceptional in that it reduced the ionization current below its standing value. This might be explained by the fact that Ne is the only gas having an ionization potential (21 eV) higher than the metastable energy of helium (19.8 eV).

A check on the accuracy of the flowmeter train was made using the equipment for the chromatographic analysis apparatus. The helium stream with v.p.m. additions of air from the flowmeter train was passed through the sample bore of the chromatographic sampling valve (16 in Fig. 1). Samples of this stream were introduced into the carrier stream to the column. The chromatogram obtained showed peaks of O_2 and N_2. The areas under the peaks were determined by cutting the peaks out of the chart and weighing. The areas obtained are plotted (in arbitrary units) against O_2 and N_2 partial pressures in the sample, in Fig. 6. The "T" valve (18 in Fig. 1) was then used to fill the sample bore of the sampling valve (16 in Fig. 1) with air at known low pressures as described in 3.4. Samples of this low pressure air were introduced into the column carrier stream. The areas under the O_2 and N_2 peaks of the chromatograms obtained were again determined by weighing and are plotted in Fig. 6.

Comparison of the two sets of results is made on areas which are proportional to the masses of O_2 and N_2 in the samples rather than peak heights. This was necessary because the samples from the flowmeter train were in helium at atmospheric pressure, whereas the samples from the "T" valve were under vacuum. Slightly different peak widths were obtained in the two sets of results, and comparison of the areas for the two methods of making up the samples showed that the differences had standard deviations of 5 % for O_2 and 6 % for N_2.

These standard deviations are about the expected values, considering that each of the flowmeters in the train had a standard deviation of 2 %. In calculating the v.p.m. additions made by the train, eight flows were multiplied and divided together. Elementary statistics show that the result should have a standard deviation of $\sqrt{8} \times 2\%$ or 5.7%.

In view of this, the standard deviation of the calibrations on Fig. 6 cannot be considered better than about 6 % even though the actual points plotted show a smaller deviation. This is due to the way the flowmeter train was operated to give different v.p.m. additions by varying only one or two flowmeters while the others remained constant, instead of randomising all values.

The stability of the detector standing current may now be assessed in terms of v.p.m. additions of other gases to the purified helium. From Fig. 4 it is evident that
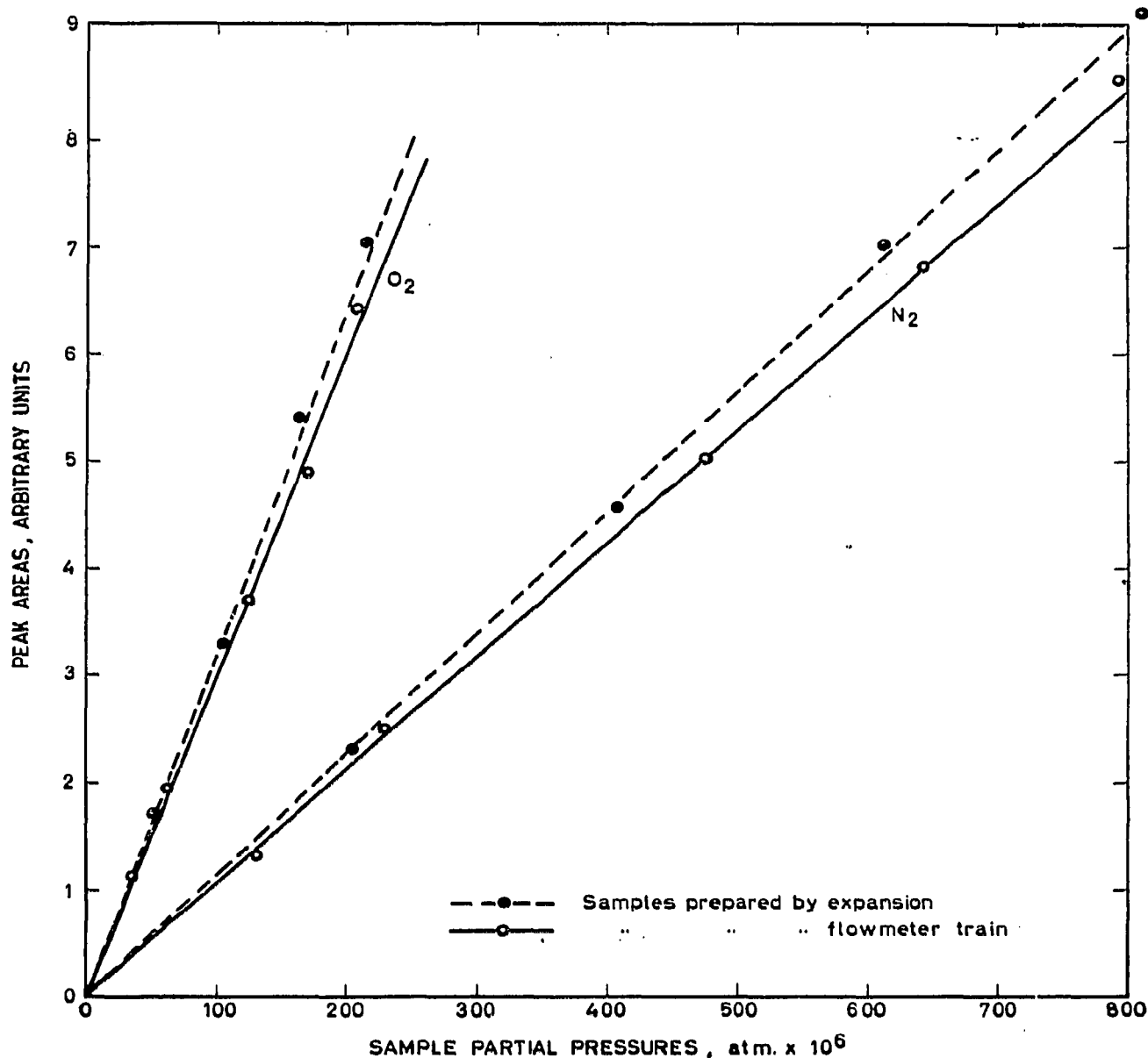
Fig. 6. Comparison of chromatograms of samples prepared by expansion and by flowmeter train.

the short term stability is such that an abrupt change in ionization current of 1.4×10^{-11} amps (one scale division) significantly indicates a change in the v.p.m. of other gases in helium stream. The v.p.m. of various gases equivalent to 1.4×10^{-11} amps change (taken from Fig. 5) are:

CO_2	CH_4	CO	O_2	A	N_2	H_2	Ne
0.02	0.05	0.06	0.07	0.15	0.2	0.5	1.0

These are the minimum significantly detectable v.p.m. changes of other gases in the purified helium.

The results given in Figs. 4 and 5 were obtained from the detector used for the liquid helium experiment (4.3) using an outlet from the flow meter train not shown in Fig. 1.

4.3 Helium purity

Before carrying out the liquid helium experiment to investigate the purity of the helium gas from the purifier it was necessary to establish that the trapping efficiency and capacity of the liquid helium cooled coils (12 in Fig. 1) were adequate to reduce to sufficiently low levels all other gases which might remain in the purified helium. The saturated vapour pressures of permanent gases were extrapolated to 4°K, using the Clausius-Clapeyron equation. This showed that, if equilibrium was attained in the coils, H_2 and Ne ratios in the helium at one atmosphere would be reduced to about 10^{-5} v.p.m. and 10^{-9} v.p.m., respectively, and ratios of all other gases would be quite negligible. Equilibrium may not, however, be attained because nucleiation of impurities in the gas may result in solid aerosol particles blowing through the coils and re-evaporating on warming downstream. The trapping efficiency and capacity of the coils had therefore to be determined experimentally. This was done by filling the dewar (11 in Fig. 1) with liquid helium to cover the coils. After temperatures and the purified helium gas flow had steadied, the standing current of the ionization detector was noted. Then, using the flowmeter mixing train, additions up to 50 v.p.m. of various gases were made to the purified helium stream before the coils for periods up to one hour. For no gas, at any v.p.m., was there any detectable change in the standing current. It was therefore concluded that the liquid helium cooled coils had adequate efficiency to remove all other gases from the helium to at least as low as the minimum detectable changes (4.2). The capacity of the coils was also shown to be more than sufficient to hold all the gases which were removed from the purified helium during an extended run.

After the trapping performance of the coils had been checked, the first part of the liquid helium experiment was begun by recording (Fig. 7) the standing current of the ionization detector for the purified helium passing through the coils at room tempera-
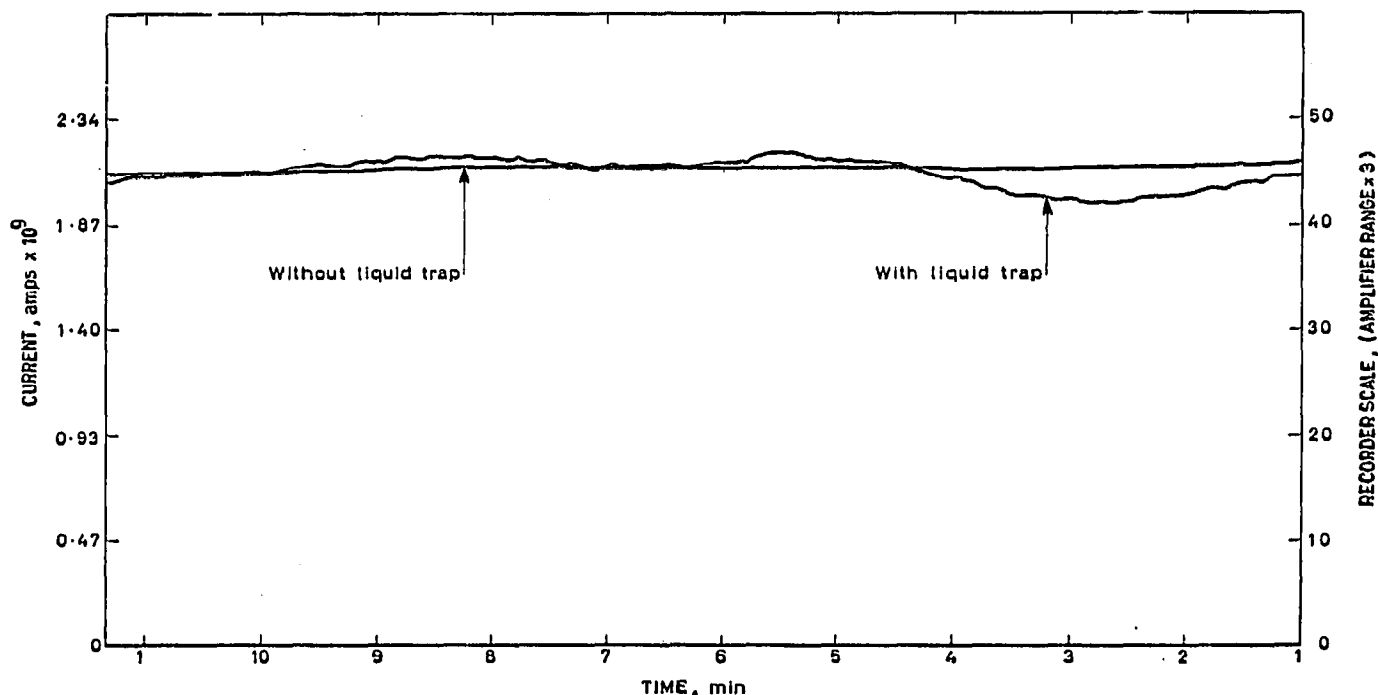

Fig. 7. Standing current with and without liquid helium trap.

ture. The coils were then cooled to 4°K and the standing current was again recorded on the same chart (Fig. 7) at the same pressure, temperature and flow rate. The line on Fig. 7 for the coils at room temperature shows the usual stability of the standing current. The line for the coils at 4°K has considerably greater fluctuations. These seemed to be caused by pressure and flowrate variations of the gas stream induced by even the smallest draughts in the laboratory near the gas stream outlet. They occurred when the coils were at 4°K and only slightly above ambient pressure (to prevent liquefaction of the gas by the liquid helium). It was probable that pressure and flowrate surges may have been the result of pressure variations downstream causing slight displacement through the large temperature gradients along the glass tubes dipping into the liquid helium of the large mass of gas near saturation and at about 1000 times its normal density held up in the coils.

Treating the differences between the two lines on Fig. 7 statistically, the liquid helium standing current has an average value 1.9×10^{-11} amps less than the room temperature value and the standard deviation of the difference between the lines is 6.1×10^{-11} amps. Hence the difference between the lines is not significant and may have been due to the fluctuations mentioned above. Taking twice the standard deviation as significant and the calibrations of the detector (Fig. 5) for various gases, it is concluded that the liquid helium cooled coils cannot have removed from the purified helium more than any of the following v.p.m. of other gases separately:

Ne	H_2	N_2	A	O_2	CO	CH_4	CO_2
7.6	3.6	1.4	1.3	0.5	0.5	0.4	0.1

To specify upper limits to the v.p.m. of other gases in the helium before the 4°K trap the minimum detectable changes (see 4.2) must be added to these values, because the trapping efficiency of the coils were not proved better than these changes. This gives the v.p.m. upper limits as:

Ne	H_2	N_2	A	O_2	CO	CH_4	CO_2
8.6	4.1	1.6	1.5	0.6	0.6	0.4	0.1

The second part of the liquid helium experiment was an attempt to determine the actual values of the v.p.m. of the individual gases below these limits. In it the liquid helium run was extended up to five hours. After this time the two diaphragm valves shown on Fig. 1 before and after the coils were closed to isolate their contents of helium and trapped gases. The downstream section of tubing was next evacuated and closed under vacuum by the diaphragm valve immediately after the chromatographic sampling valve (16 in Fig. 1). The coils were then opened to this evacuated section, warmed to room temperatures and left for an hour to allow the trapped gases to evaporate and mix uniformly with the helium. The final helium pressure in this closed volume was about $1/10$ atm. The volume of helium passed through the coils during the run was about 150 times the closed volume. The final pressures of the trapped gases were, therefore, about 150 times the reductions in these pressures achieved by the coils during the run. To be more accurate the final impurity pressures, in addition to the 150 times amplified reductions, also included $1/10$ of the impurity pressure remaining in the helium after passing through the coils. These corrections although unknown cannot however have been more than $1/10$ of the minimum detectable changes and are negligible in comparison with the 150 fold amplification.
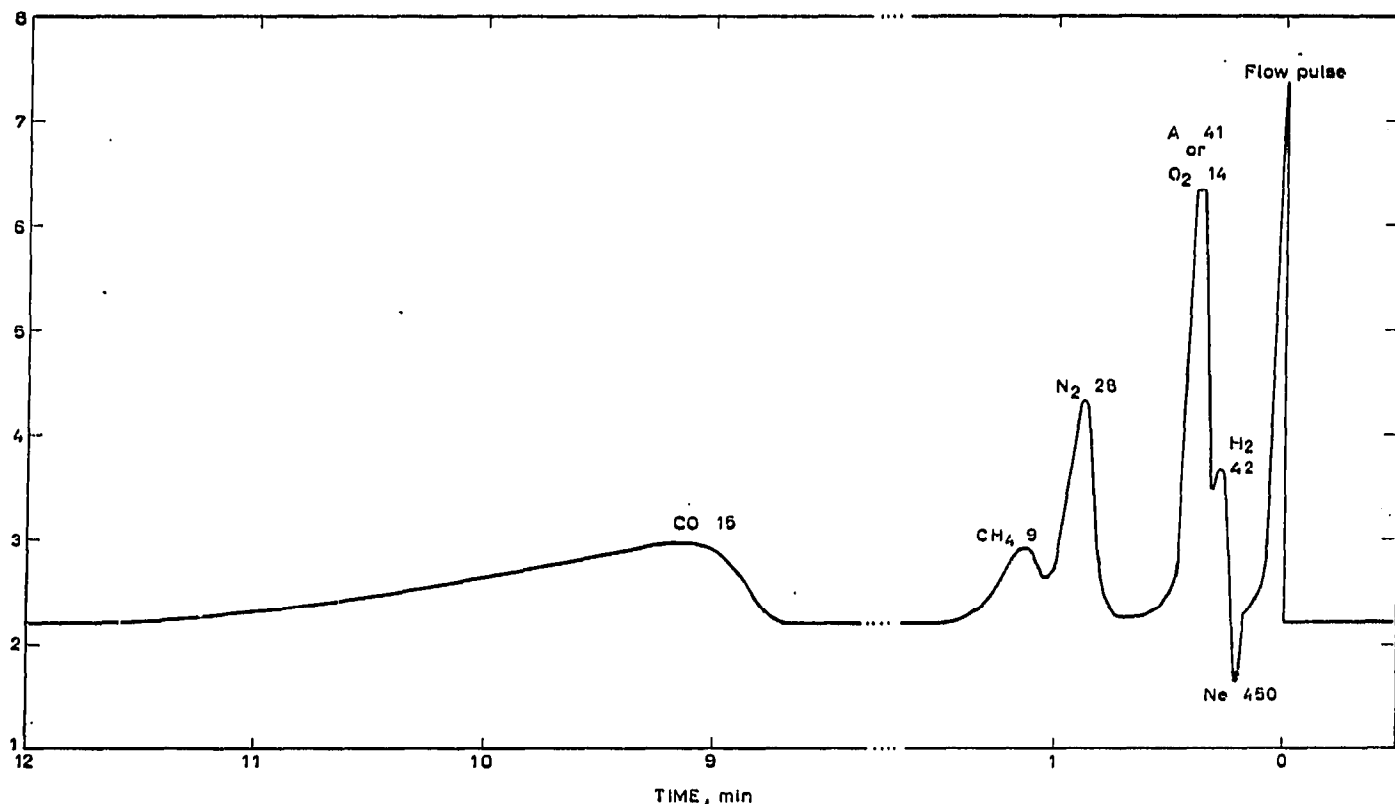
Fig. 8. Chromatogram of liquid helium trapped impurities showing their partial pressures (atm. × 10⁻⁶) in sample.

Mass spectrometric and gas chromatographic analyses were made of the final mixture of helium and amplified impurities. Samples for the former were taken in the breaker seal tubes (22 in Fig. 1). A sample for the latter was injected by the chromatographic sampling valve into the carrier stream to the room temperature molecular sieve column (19 in Fig. 1). The chromatogram obtained is reproduced in Fig. 8. The partial pressures in p.p.m. of one atmosphere of the various impurities in the sample were determined by calibration, using the flow meter train and are marked on Fig. 8. Peaks were observed for Ne, H_2, A or O_2, N_2, CH_4 and CO. CO_2 would not have passed through the molecular sieve at room temperature.

From the results of the two analyses the v.p.m. of the various gases removed from the helium passing through the 4°K trap were calculated to be:

	Ne	A	O_2	N_2 + CO	H_2	CH_4	CO_2
Mass spectrometry	4.5	0.7	<0.01	0.4	0.5	<0.01	<0.01

	Ne	A or O_2	N_2	CO	H_2	CH_4	
Gas chromatography	3	0.3 or 0.1	0.2	0.1	0.3	0.005 –	

	Ne	A	O_2	N_2	CO	H_2	CH_4	CO_2
Averages (rounded)	4.0	0.5	<0.01	0.3	0.1	0.4	0.005	<0.01

N_2 and CO could not be discriminated in a mass spectrometer because of their similar molecular weights. A and O_2 could not be separated in the column because of their similar adsorption isotherms on room temperature molecular sieve.

Comparing the two sets of results there is reasonable agreement between them. The average value of each gas may, therefore, be taken as an estimate of its v.p.m. in the helium from the purification train before entering the 4°K coils if these coils are assumed to have trapped each gas to substantially less than this v.p.m. This assumption could not be proved (in the test mentioned at the beginning of 4.3) in the case of CO_2, CH_4, CO and O_2 because the estimates of their v.p.m. are less than the minimum detectable values and they might not have been efficiently trapped. Although this seems unlikely because no break through the coils was observed for inlet v.p.m. from the minimum detectable changes up to at least 50 v.p.m., to be accurate, the minimum detectable changes (see 4.2) must be added to the average values to specify upper limits to the concentrations of the various gases remaining in the helium from the purification train. This gives these v.p.m. as:

Ne	A	H_2	N_2	O_2	CO	CH_4	CO_2
5	0.7	0.8	0.5	<0.08	<0.07	<0.05	<0.03

The whole of this liquid helium experiment was carried out three times using different cylinders to supply the helium gas for purification. The results for N_2, H_2, O_2, CO, CH_4 and CO_2 were closely the same each time. The A ratios varied from 0.3 to 1.0 v.p.m. and the Ne from 3 to 5 v.p.m. The A would have been reduced only by the — 196° molecular sieve traps in the purifier and the Ne would not be changed by any of the purifier stages. These differences were therefore probably due to variations in the supply.

5. CONCLUSIONS

From the results of 4.3 it is concluded that the gas purification train described is capable, without the use of a final liquid helium trap, of providing a helium stream containing less than the following v.p.m. of other gases:

CO_2	CH_4	CO	O_2	N_2	A	H_2	Ne
0.03	0.05	0.07	0.08	0.5	0.7	0.9	5.0

The results of 4.2 show that when various gases are added to the purified helium, the minimum significantly detectable v.p.m. changes are:

CO_2	CH_4	CO	O_2	N_2	A	H_2	Ne
0.02	0.05	0.06	0.07	0.2	0.2	0.5	1.0

Detection by this technique of any of these gases in a helium chromatographic stream down to their minimum significantly detectable v.p.m. is therefore possible subject to constant negative errors of their v.p.m. remaining in the helium stream and to random fractional errors of 6% standard deviation due to the method of calibration.

SUMMARY

A technique is described for analysing volume parts per million (v.p.m.) mixtures of permanent gases in helium using the Lovelock radioactive ionization detector after chromatographic separation. The amounts of all other gases remaining in a carefully

purified helium carrier stream were proved using a liquid helium trap to be less than 1 v.p.m. (except neon, 5 v.p.m.), varying from 0.03 v.p.m. CO_2 to 0.9 v.p.m. H_2. The accuracy of the technique is specified down to the limits of significant detection, ranging from 0.02 v.p.m. CO_2 to 0.5 v.p.m. H_2.

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