A device for transferring small volumes of gas from a vacuum line to a gas chromatograph

Various techniques have been developed for introducing vapour samples into gas chromatographic instruments[1–5]. However, none of these methods is particularly suitable for transferring small volumes of gas from a vacuum line. The apparatus described below has been designed to be used in conjunction with one or more Ward Stills[6] and a gas chromatograph in order to analyze quantitatively the very small amounts of gases produced during the radiolysis of organic compounds. It can also be used whenever it is necessary to measure and transfer small amounts of gas from a vacuum line to a gas chromatograph.

The essential part of the apparatus, which is shown in Fig. 1, consists of a combined Toepler pump (T), McLeod Gauge (M), gas burette (G) and sample injection device (I). This apparatus is connected by a Ward Still (W) to the part of the vacuum

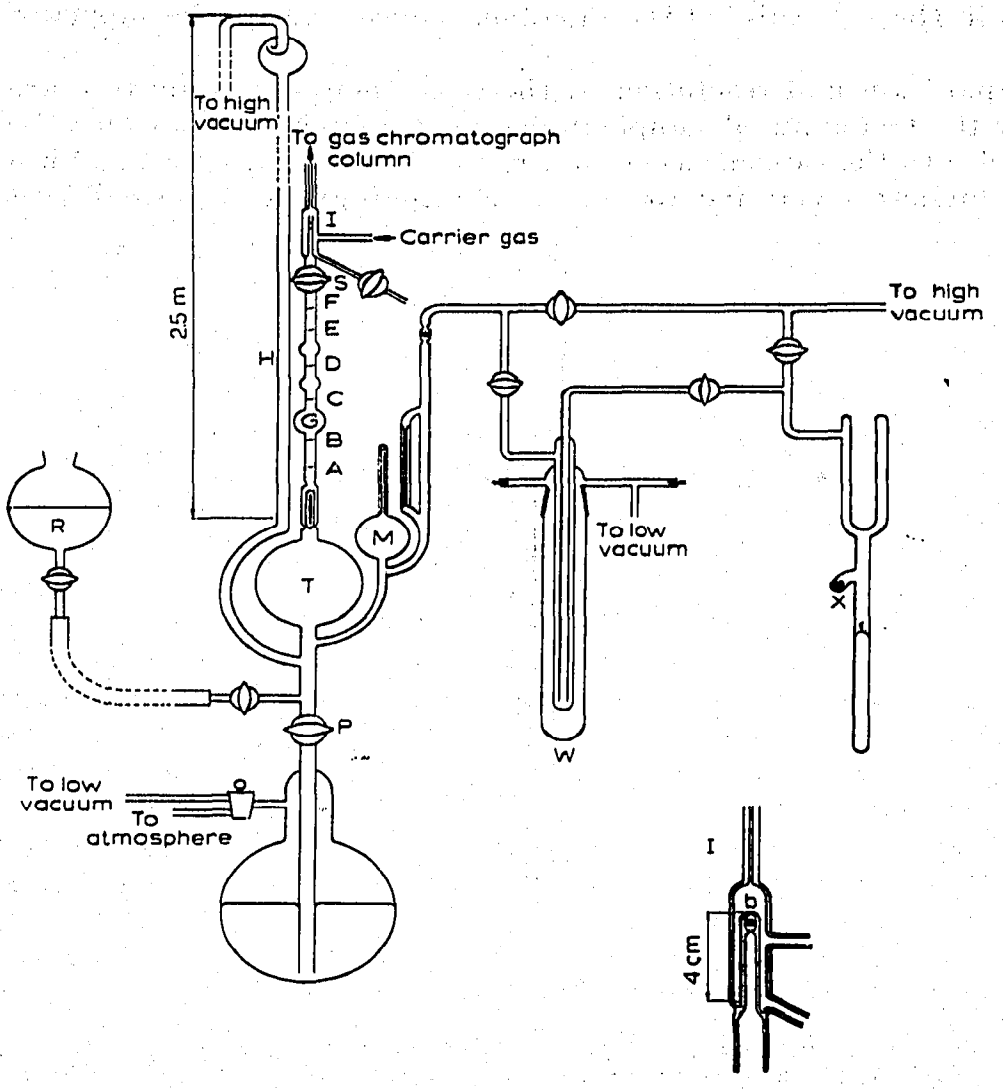

Fig. 1. Apparatus used for the separation, measurement and injection of gases into a gas chromatograph. The injection device is shown in the enlarged section. Calibrated volumes in the gas burette are S–A 5.89 ml, S–B 5.60 ml, S–C 2.29 ml, S–D 0.83 ml, S–E 0.18 ml, S–F 0.12 ml.

line which contains the gas to be analyzed. The gas sample injection device, which is shown in detail, is connected to the column of the gas chromatograph by about 1.5 m of 1 mm capillary tubing.

The gas chromatograph was calibrated by introducing known volumes of various gases from the vacuum line. A sample of gas was pumped into one of the calibrated bulbs of the gas burette by the Toepler pump. The difference in height between the mercury in the tube (H) and the appropriate calibration mark in the gas burette (G) was noted. The mercury reservoir (R) was then raised to such a height that the gas in (G) was compressed to a pressure greater than that of the carrier gas stream. In this particular case, the level of mercury in the tube (H) was some 1.5 m above the stopcock (S). The stopcock (P) was closed and the stopcocks connecting the Toepler pump to the mercury reservoir were opened. With a suitable carrier gas sweeping through the injection device, the stopcock (S) was then opened. The sample of gas, at high pressure, was thereby injected very rapidly into the stream of carrier gas, mercury being largely held back by the ball bearing (b). Any mercury which may escape past (b) collects in the side tube of the injection device and can be tapped off at a later stage.

The separation and resolution of the components of a mixture are greatly influenced by the technique of sample injection. The high rate at which the gas sample was injected into the carrier gas stream resulted in only a very small injection peak, even at the highest sensitivity used on the chromatograph. The small internal volume

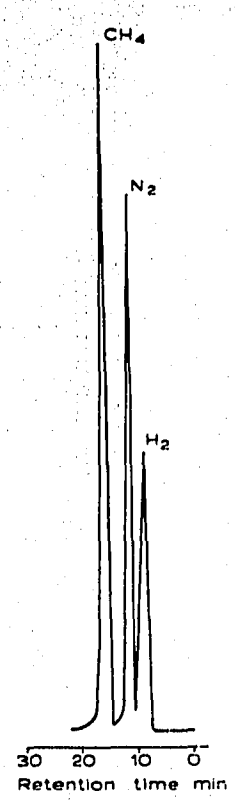

Fig. 2. Curve obtained from a sample of gas containing methane, nitrogen and hydrogen. Between the hydrogen peak and the nitrogen peak the sensitivity was reduced by a factor of 10. A six-foot silica gel column was used at room temperature with argon carrier gas flowing at a rate of 10 ml per minute. The chromatograph used was the Pye Gas Chromatograph with the katharometer detector.

of the injection device and the capillary connection with the column in the chromatograph successfully prevented any broadening of the peaks. A typical curve is shown in Fig. 2. Using samples of pure gases and also mixtures of gases which had been analyzed by other methods, calibration curves were prepared for each component present in the sample of gas which was to be analyzed. The reproducible way in which small samples of gas can be injected into the chromatograph is indicated by the straight lines obtained in the calibration curves; typical examples are shown in Fig. 3.

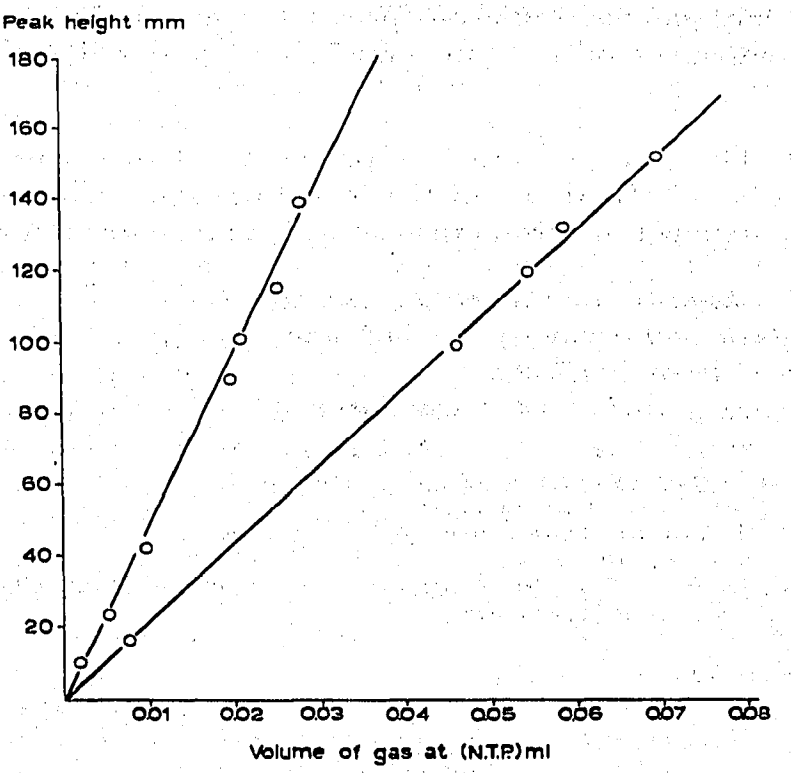

Fig. 3. Calibration curves obtained for pure hydrogen at two different sensitivities of the gas chromatograph. A six-foot silica gel column was used at room temperature with argon carrier gas flowing at a rate of 10 ml per minute.

The analysis of a complex mixture of gases may require the use of more than one column packing or carrier gas. It may be necessary, therefore, to fractionate the gas mixture, holding back certain fractions until the column of carrier gas has been changed. The low temperature fractionation of small gas samples has been described by LE ROY[6] and this method, employing a Ward Still, has been used in the present work. The same technique was applied when analyzing the small amounts of gases produced when certain organic compounds were subjected to ionizing radiations. A known volume of an air-free organic liquid was enclosed in a sealed tube fitted with a break-seal and irradiated with X- or gamma-rays. After irradiation, the tube was sealed into the vacuum line at point (X), evacuated and the break-seal was broken. The temperature inside the Ward Still, which was immersed in liquid nitrogen, was adjusted by means of the built-in heating coil so that the irradiated organic liquid was just held back. The less condensible gases produced during the radiolysis were then pumped into the gas burette until the pressure in the vacuum line had fallen to 10^{-2}

to 10^{-3} mm as indicated by the McLeod gauge. The gas sample was then measured and injected into the gas chromatograph.

Using this apparatus, it was found that volumes of gases between 0.04 ml and 1.0 ml at N.T.P. could be analyzed. The usual size of gas sample produced by the radiolysis of organic compounds was, in the present work, of the order of 0.1 ml. It was found that this could be separated and that each component could be analyzed quantitatively, the accuracy of the analysis being dependent on the size and composition of the sample. In a typical experiment where methyl cyanide was irradiated with gamma-rays, the only gaseous radiolysis products were shown to be methane and hydrogen: each component in a 0.1-ml sample was analyzed with an accuracy of $\pm$ 5%.

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Paper chromatography of some 2,4-dinitrophenyl S-alkyl-(L)-cysteines and corresponding sulfoxides

Recently we reported on the isolation of (+)S-methyl- and (+)S-*n*-propyl-(L)-cysteine sulfoxides from the onion (*Allium cepa*) as 2,4-dinitrophenyl derivatives[1]. In the course of this work, derivatives of some other S-alkyl-(L)-cysteines were also synthesized and studied. Before these compounds could be isolated in pure form by silicic acid chromatography, it was necessary to determine their chromatographic behavior and the feasibility of separating them from neutral amino acids obtained coincidentally from onion extracts.

This report describes the paper chromatography of the N-2,4-dinitrophenyl derivatives of these amino acids. Chromatography of N-2,4-dinitrophenylamino acids[2] has been widely used in end-group determinations of proteins and peptides and composition of protein hydrolysates[3]. The highly colored derivatives are easily detected on the chromatograms and can be eluted and measured colorimetrically[4,5].