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Note

Simple modification of a gas chromatograph for radio-assay of tritium-labelled compounds

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The rapid estimation of tritium in the components of mixtures of labelled compounds of sufficient volatility may be achieved by radio-gas-liquid chromatography. The instrumental techniques developed for this method of analysis and examples of the application of the procedure have recently been reviewed^{1,2}. Much of the emphasis in the adaptation of radiation detectors for this purpose was placed on maximisation of sensitivity for compounds of low specific activity.

The recent development of ³H NMR spectroscopy^{3,4} for determination of the position of tritium in molecules has created a different need, namely, for radiochemical analysis of mixtures with components of high specific activity. Typically, samples containing 10–30 mCi of radioactivity in volumes of the order of 0.05 ml are prepared for ³H NMR analysis from material used in studies such as surface catalysis^{5,6} or biosynthesis⁷. Such samples have radioactivities sufficiently high for detection by simple ionisation chambers, and thus more complex and expensive methods based on proportional, scintillation, or solid state detector systems are not necessary. We have therefore investigated the very simple adaptation of the second flame ionisation detector of an existing dual detector gas chromatograph as an ion chamber type.

EXPERIMENTAL

As with many commercial gas chromatographs, the available instrument contained two identical flame ionisation detectors, a variable post-column splitter and dual pen recorder, but only a single differential type electrometer. The only significant addition necessary to the system consisted of a second electrometer capable of measuring currents of the order of 10^{-12} A at full scale deflection. A vibrating reed instrument has proved to be ideal for this purpose. Had a second independent electrometer of adequate sensitivity been supplied with the chromatograph this addition would not have been required.

Modifications were made to the second flame ionisation detector of the instrument as follows: (1) The polarising voltage cable to the flame ionisation detector was removed; (2) the input socket to the jet was grounded to the outer case of the flame

ionisation detector; (3) the cable to the igniter terminal on the flame ionisation detector was disconnected; (4) the signal cable was removed from the collector electrode socket on the flame ionisation detector and replaced with a short length of low capacitive co-axial cable to connect the collector to the input of the vibrating reed electrometer; (5) the post-column splitter was arranged such that 10% of the carrier gas from the column passed to the first flame ionisation detector and 90% to the modified flame ionisation detector; (6) the modified detector operating as an ion chamber was run with no hydrogen flow but with approximately normal air flow to act as a purge gas.

The polarising potential necessary for the ion chamber operation was supplied from a dry cell battery connected between the grounded outer case of the modified flame ionisation detector and the input screen of the electrometer. It is essential that the design of the electrometer input circuit permit elevation with respect to ground of its input stages by at least the magnitude of the polarising voltage. Tests indicated that 15 V polarising potential was adequate to obtain saturation current within the ion chamber.

The performance of the instrument was checked by preparing a tritiated mixture. A 0.3-ml volume of a mixture of benzene, toluene and xylene was placed in a narrow glass tube to which 10 mg of pre-reduced PtO_2 was added, followed by 5 μl of ^3HHO (50 Ci ml^{-1}). The tube was cooled in liquid nitrogen, evacuated and sealed before heating at 90°C for 24 h. After cooling the tube was opened, the liquids extracted into ether (2 ml) and washed with water (1 ml) before drying with anhydrous sodium sulphate. The ether was gently removed by passing a stream of nitrogen through the solution. The solution was then diluted with 1 ml of an inactive mixture of benzene, toluene and xylene. The total radioactivity came to 45 mCi which made it possible to use 1- μl samples (45 μCi) of the mixture in the chromatographic studies.

RESULTS AND DISCUSSION

The modifications described above are elementary and easily reversed, and require no more than a few minutes to perform. The essential features of the electrical circuitry are shown in Fig. 1. The ion current is collected between the cylindrical

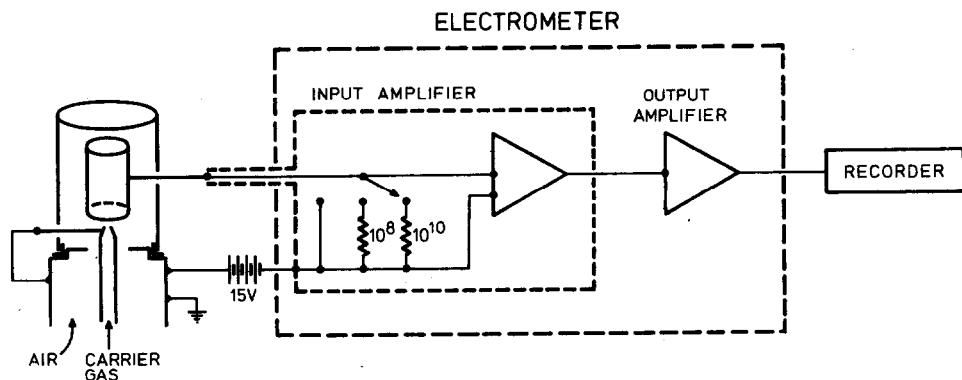


Fig. 1. Modified flame ionisation detector and electrometer input schematic diagram.

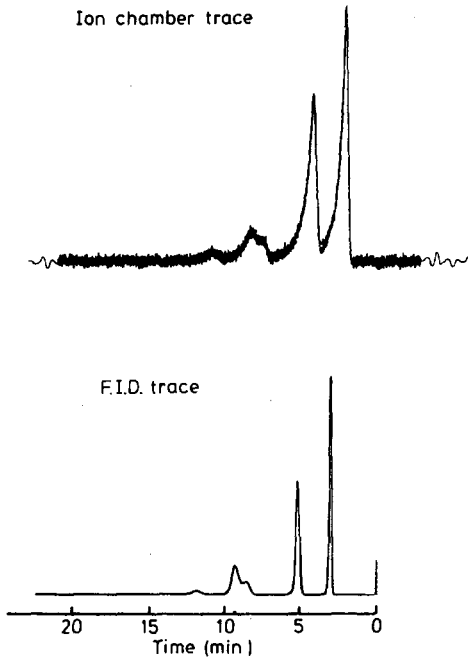


Fig. 2. Flame ionisation detector and ionisation chamber traces for a mixture of [G-³H]-benzene, -toluene and xylene.

collector electrode of the modified flame ionisation detector and its outer case. It is measured as a voltage drop in the range 10–1000 mV across an input resistor in the electrometer which could be selected in the range 10^8 – 10^{10} ohms. Typical results for the prepared tritiated mixture are given in Fig. 2. Clearly the amount of radioactivity associated with each component is proportional to its concentration, a result that

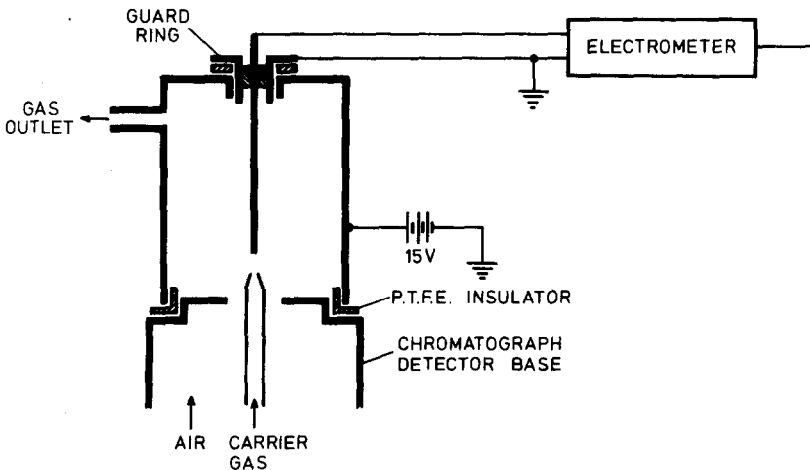


Fig. 3. Design of ionisation chamber with guard ring for possible replacement of chromatograph flame ionisation detector.

could have been anticipated as under the experimental tritiation conditions equilibrium would have been reached. The xylene used was clearly a mixture of isomers, all of which have been labelled. Under the most sensitive conditions samples containing as little as 1 μCi could be analyzed. The flow-rate of the purge gas was usually chosen such that sensitivity remained adequate and there was no significant loss of resolution of components within the volume of the detector. Ion chambers are subject to slight changes in efficiency when their gas composition is modified by the components emerging in the chromatograph effluent. This phenomenon can be minimised when sample activities are sufficiently high to allow for increased purge gas flow-rates without decreasing the sensitivity limit of the chamber below the sample activity.

The ease with which an existing gas chromatograph may be adapted to radioactivity measurement, and, if an electrometer is available, the negligible cost, are attractive features. Where higher sensitivity is required, the electrode and case assembly of the flame ionization detector can be replaced by a specially constructed chamber (Fig. 3) designed to fit the flame ionisation detector base of the chromatograph. It consists essentially of a single rod as central electrode and a cylindrical chamber which is insulated electrically from the chromatograph detector base. This construction, including the provision of a guard ring around the central electrode, would permit the use of a higher sensitivity electrometer with up to a 10^{12} ohm input resistor. Electrical leakage currents would be minimised and the electrometer would operate with input return at ground potential since the polarising voltage would be applied to the outer chamber wall as indicated in Fig. 3.

Ion chamber methods of tritium assay have the considerable advantage that outlet stream combustion and reduction tubes used in the more common proportional counter for gas chromatography tritium analysis^{1,2} are not necessary. The input may be rapidly energised without the need for packing and heating of silica combustion tubes which themselves frequently introduce memory effect problems and high backgrounds due to inadequate operation. Furthermore, where purification of a compound is the objective the system described is ideal for adaptation to a preparative scale gas chromatograph. A disadvantage of the instrument is that differential dual flame ionisation detection is not possible while one of the two detectors is in operation as an ion chamber. Thus temperature-programmed analyses in some circumstances may yield changing base lines on the flame ionisation detection output trace.

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