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Note

Simple gas-loop injection system for use with capillary columns

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Considerable effort has been expended in recent years in attempts to extend the usefulness of capillary gas–liquid chromatography (GLC) for the study of relatively involatile compounds. This effort has resulted in the development of on-column injectors in order to avoid the need for sample vapourisation. Correspondingly little research has been performed to exploit the potential of capillary GLC for the analysis of volatile compounds and gases. Such a capability is, however, particularly important for areas of application such as food and flavour research, perfume and fragrance research, environmental control measurements, for example measurement of the trihalomethane content of potable waters, and the concentrations of industrial solvents, *e.g.* 1,1,1-trichloroethane, in closed working environments.

The application of capillary GLC to the study of gases and volatile compounds necessitates two particular requirements, *viz.* a simple and reliable means of injecting a known and reproducible volume of sample gas onto the column and a column with sufficient retention to facilitate the separation of such compounds as methane from ethane, methanol from ethanol and dichloromethane from chloroform.

Injection techniques which have been used fall into two categories: preconcentration systems[1-6] and direct injection systems[7-11]. Preconcentration techniques are time consuming and accumulate interferents and contaminants as well as components of interest. The direct injection systems which have been reported are primarily intended for use with packed columns[7,9] and thus utilise large sample volumes (*e.g.* ref. 7). The simplest direct injection system, the gas-tight syringe, is relatively imprecise in its ability to measure volumes reproducibly.

For precise quantitative work and user convenience a direct injection system employing a valve loop injector is required. In this paper we describe the use of a Rheodyne high-performance liquid chromatographic (HPLC) loop injector (Model 7010) as a gas sampling valve for capillary GLC.

EXPERIMENTAL

A Carlo Erba (Swindon, U.K.) Fractovap 2450 series chromatograph modified by addition of a Grob type split/splitless injector for capillary GLC was used. Columns (40 m × 0.25 mm I.D.) coated with either OV-101 or Reoplex 400 (25 m × 0.25 mm I.D.) (HCl etch, Carbowax 20M deactivation) were connected to the injection port (200°C) and the detector (micro-volume electron capture; Model 251, Carlo

Erba) which was maintained at 200°C. A purge through the detector of 30 ml min⁻¹ nitrogen was used. The split ratio for the injector was set to 1:10 and the valve injector fitted as in Fig. 1. Flow-rate (valve injector): 2.5 ml min⁻¹. Flow-rate (column): 1.5 ml min⁻¹. Oven temperature: Fig. 2, 60°C; Fig. 3, 25°C.

Standard mixtures were prepared by weighing known amounts of compounds into glass vessels (200–500 ml) fitted with greaseless vacuum taps. The vessels were used either as containers for water samples or as sample collection vessels for vapour samples. Further dilution with air was necessary to provide standards suitable for use with electron-capture detection.

RESULTS AND DISCUSSION

More retentive capillary columns may be prepared by coating thick films of liquid phase (*ca.* > 0.5 μm) onto the capillary column wall[12]. The loss of column efficiency caused by use of a film of this thickness is of little consequence because there are relatively few possibilities for the co-elution of compounds. For example, in natural gas, there is very little possibility of a compound eluting between methane and ethane. Hence the column need only be able to resolve methane from ethane sufficiently well to tolerate a methane/ethane ratio of about 10:1. We have found thick film capillary columns to be particularly useful in the study of volatile compounds.

Equipment

The use of the Rheodyne valve as a gas loop injection device for capillary GLC is illustrated in Fig. 1. Flow through the valve is set by the needle valve with typical flow-rates being 2 ml min⁻¹. The valve is fitted with a 20-μl loop. A piece of fused silica (approx. 20 cm) is connected to the valve using a conventional nut and PTFE ferrule. The free end of the fused silica is threaded through the septum. The positioning of the end of the fused silica with respect to the end of the column in the
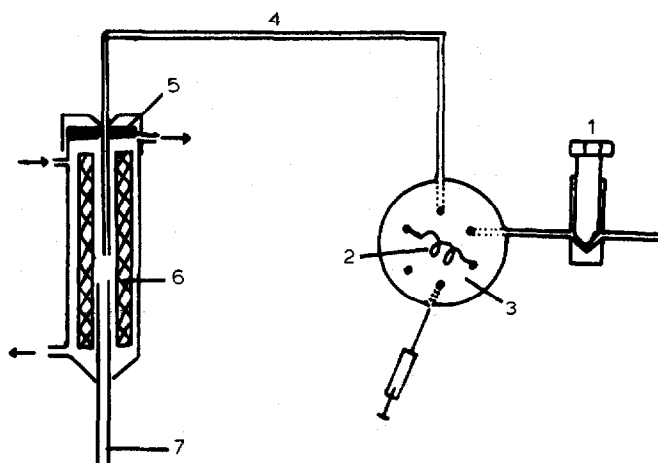

Fig. 1: Schematic diagram of the gas loop injector device. 1 = Needle valve; 2 = 20-μl loop; 3 = Rheodyne Model 7010; 4 = flexible silica; 5 = septum; 6 = glass liner; 7 = capillary column.

injection port controls the efficiency of sample transfer*. Normally the system is operated in the split mode but with a split ratio of only 1:10. Clearly this represents a considerable loss of sensitivity over that which is theoretically possible. Although it has not been attempted by us, it seems logical to anticipate that the introduction of the flexible inlet capillary inside the column will permit on-column injection of volatile compounds with a corresponding increase in sensitivity. However, the system described is sufficiently sensitive to allow the direct determination of trihalomethanes in water by injection of 20 μl of headspace vapour (see below).

Contamination studies

        Difficulties arising from contamination and memory effects from the rotor seal in the valve were anticipated. Sample carry-over was prevented by flushing the loop at least three times with air between injections. The material of the rotor was thought to be a fluoropolymer. Thus an electron-capture detector was used to check for contamination. Injections of "clean" air revealed only one large, poorly retained peak attributed to oxygen passing through the detector. Laboratory air was contaminated with a low level of dichloromethane presumably because other workers were using this as an extracting solvent. Operation of the valve *without* filling the loop produced no spurious response (and no oxygen peak). An injection of an air sample containing chloroform followed by an injection of "clean" air after flushing the loop produced no "ghost" peak of chloroform. In many weeks of use no evidence has been observed that this valve injection system either adds to, or subtracts from, the samples that have been injected.

Applications

        This combination of micro-gas loop injection and a thick-film capillary column has been used to study many analytical problems. In particular we have studied trihalomethanes in tap water, residual anaesthetic gas (Halothane) levels in operating theatres, natural gas composition, natural gas condensate composition, solvent vapours in the industrial working environment and identification of solvents of abuse.

        Fig. 2 shows three chromatograms which illustrate the usefulness of this approach to the study of the trihalomethane content of drinking water. Fig. 2A shows the chromatogram of an injection of 20 μl of headspace vapour from double distilled water. Fig. 2B shows a standard mixture of trihalomethanes in air. Fig. 2C is the chromatogram obtained from the headspace above ordinary tap water and shows clearly the presence of $CHCl_3$, $CHCl_2Br$ and $CHClBr_2$. Preparation of standard mixtures of chloroform in double distilled water suggests a detection limit of 2 ppb for this compound.

        Recently, considerable concern has been expressed about the abuse of solvents such as toluene. Identification of the solvent in question is normally achieved by packed-column gas chromatography[13] involving temperature programming and giving a chromatographic analysis time of 25 min. Using capillary GLC this time is much reduced. A separation of the six commonest solvents of abuse is shown in Fig. 3. To obtain this sample a mixture of the six components of interest was equilibrated

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* The glass liner has an internal diameter of only 1.1 mm to assist alignment of the fused-silica inlet line with the capillary column and thus assist in sample transfer.
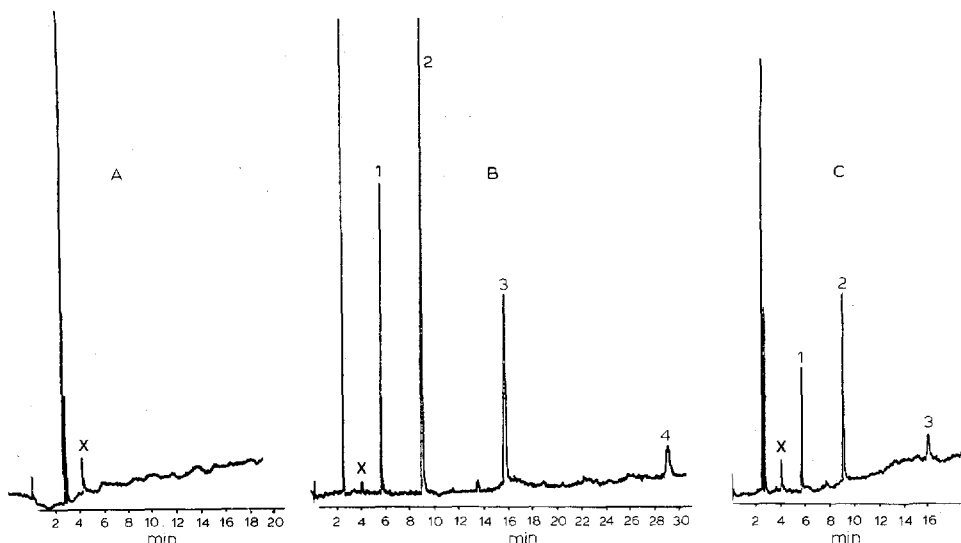
Fig. 2. (A) 20-μl injection of headspace vapour from double distilled water (*i.e.* a blank sample) maintained at 90°C. X = CH$_2$Cl$_2$. (B) 20-μl injection of standard mixture of trihalomethanes in air. Peaks: 1 = CHCl$_3$, 2 = CHCl$_2$Br, 3 = CHClBr$_2$, 4 = CHBr$_3$. X = CH$_2$Cl$_2$. (C) 20-μl injection of tapwater headspace vapour (water temperature 90°C). Peaks: 1 = CHCl$_3$; 2 = CHCl$_2$Br; 3 = CHClBr$_2$. X = CH$_2$Cl$_2$. Column OV-101 (40 m × 0.25 mm); 1 μm film thickness.
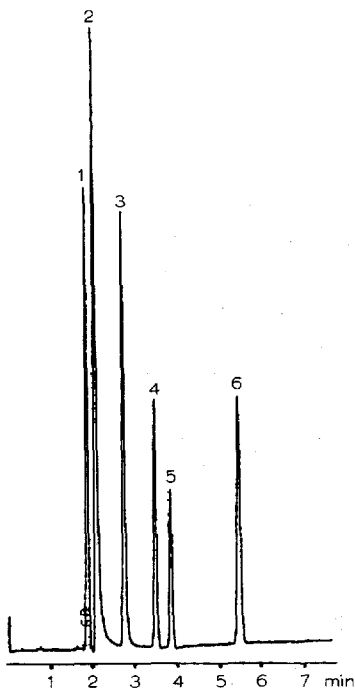

Fig. 3. Separation of the six commonest solvents of abuse. Peak identification: 1 = 1,1,1-trichloroethane; 2 = methanol; 3 = ethanol; 4 = trichloroethylene; 5 = chloroform; 6 = toluene. Column temperature = 25°C. Chart speed 1 cm min^{-1}. Injection: 20 μl headspace split 1:10. Column: Reoplex 400 (25 m × 0.25 mm I.D.), film thickness (approx.) 1 μm.

at room temperature in a sealed vial. The sample was withdrawn using a conventional glass HPLC syringe (1 ml) fitted with a Luer needle. Approximately 1 ml of headspace vapour was withdrawn through the septum of the vial and the syringe needle placed in the loop injector. This headspace vapour was used to flush the loop and then fill it prior to injection.

In conclusion therefore this simple gas loop injection system coupled with a thick-film (1 μm) capillary column provides a useful means of studying many areas of analytical chemistry concerned with the determination of volatile compounds. It offers the twin advantages of reliability and simplicity of operation and reproducibility of injection volume. Use of capillary columns rather than packed columns to study volatile compounds and gases increases resolution, decreases interferences and greatly reduces analysis time.

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