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Short Communication

Preconcentration technique for introducing gaseous or volatile compounds into a capillary gas chromatographic column

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ABSTRACT

A convenient cryofocusing technique was developed for introducing a gas or vapour sample into a capillary column. Precise temperature control was attained at the trapping segment down to −165°C in a gas chromatographic oven by controlling the flow-rate of liquid nitrogen to the trap. Gas samples, including low-boiling compounds, such as ethane, ethylene, propane, hydrogen sulphide and methanethiol, were accurately determined by cryofocusing at −165°C and by capillary gas chromatography.

INTRODUCTION

A number of cryofocusing techniques have been applied in capillary gas chromatographic (CGC) analyses of volatile compounds to give the highest attainable resolution [1–11]. These techniques ensure a better inlet-plug profile during injection into a capillary column. Conventional cryofocusing kits are usually installed outside the oven as they are relatively large and of high heat capacity in condensation and thermal desorption processes. Moreover, the vapours thermally desorbed from the trap should be re-focused at the head of the capillary column by cooling the GC oven to −98 to −50°C with a cryogen [5–8]. These procedures may be laborious, and impractical for automated analyses with reasonable accuracy. Recently, innovative multi-dimensional high-resolution GC [12,13] and cryostat systems [14–17] have been developed to enrich minor components with wide ranges of volatility and polarity. Several kits are commercially available, but they are expensive, large and complicated in operation.

This paper describes a convenient and inexpensive cryostat system that overcomes the disadvantages of conventional techniques. The cold trap used is small, light and of a low heat capacity, and is easily installed inside any GC oven. The cryofocusing tube can be cooled to any desired temperature down to −165°C by differentially controlling the flow-rate of liquid nitrogen to the cold trap. Automatic operation was readily available for determining low-boiling compounds.

EXPERIMENTAL

Standard reagents, gases and materials

Reagents and standard gases (100 ppm) were obtained from Wako (Osaka, Japan) and GL Science (Tokyo, Japan), respectively. The gas samples were

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prepared for test by diluting the standards with air to 0.5–1.0 ppm (v/v) in Flek samplers (polyester film bags) (Ohmi Odor Air Service, Shiga, Japan).

Cryostat system

Fig. 1 shows the cryostat system. The cold trap consists of a stainless-steel "mist feeder", a PTFE cooling tube, stainless-steel connection tube and a fine sheath thermocouple. A 250 mm × 0.53 mm I.D. × 0.7 mm O.D. fused-silica tube (Supelco, Bellefonte, PA, USA) and a 250 mm × 0.53 mm I.D. × 0.7 mm O.D. Pora-PlotQ porous-layer open-tubular (PLOT) column (Chrompack, Middelburg, Netherlands), inserted through the cooling tube, were used as cryofocusing tubes for trapping low-boiling compounds. Only a 10-cm segment of the cryofocusing tube was cooled in the cooling zone. The cryofocusing tube was connected with an analytical wide-bore open-tubular column or a capillary column by using a Supelco glass seal connector.

The internal pressure of the liquid-nitrogen container drove liquid nitrogen to the cold trap. The internal pressure was generated by switching a Skinner (New Britain, CT, USA) Model 16DK1050-GB three-way solenoid valve A to introduce 2.5–5.0 p.s.i. of nitrogen gas adjusted by a pressure regulator. On the other hand, the pressure was released at a limited rate by using a Skinner Model B2DA1052-GB two-way valve B under the command of an Omron (Kyoto, Japan) Model E5BX-A temperature monitor sending quick switching signals. The temperature monitor, where a desired temperature was set, closed valve B when it detected a higher temperature than the set temperature. The flow-rate of cryogen to the trap was thus increased. On the other hand, the monitor opened valve B to reduce the flow-rate when a lower temperature was detected. The cooling time and period were programmed in the microprocessor together with the GC control parameters.

Analytical apparatus

Fig. 2 shows the major components of the analytical system. A Valco Instruments (Houston, TX, USA) Model 1/16-V-6P six-way switching valve and a 1-, 2- or 9-ml sampling loop made of stainless-steel or PTFE tubing were used for sample introduction. They were placed in an oven heated at 165 and 120°C for hydrocarbons and sulphur compounds, respectively.

For the determination of low-boiling hydrocarbons, a Hewlett-Packard (Avondale, PA, USA) Model 5880A gas chromatograph was equipped with (1) a 30 m × 0.53 mm I.D. OV-1 wide-bore

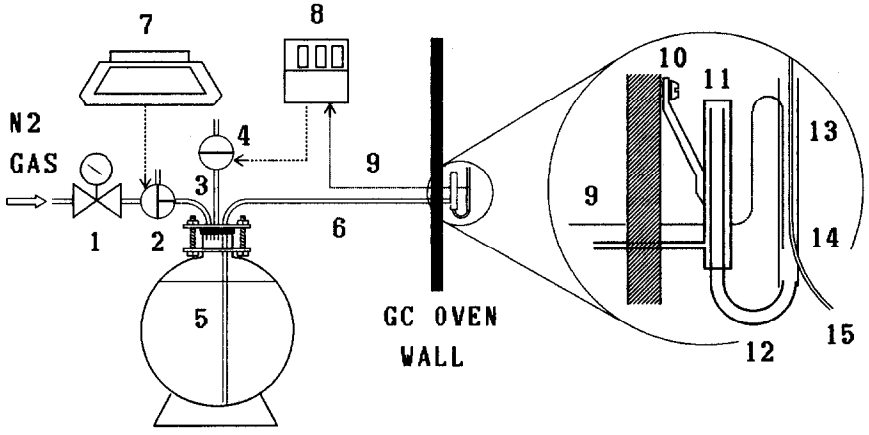

Fig. 1. Cryostat system. 1 = Pressure regulator (selectable in the range 2.5–5.0 p.s.i. according to the GC oven temperature and the desired trap temperature); 2 = three-way solenoid valve A; 3 = connection tube (2.0 mm I.D. × 3.2 mm O.D. SUS316 stainless-steel open tube); 4 = two-way solenoid valve B; 5 = 5-l liquid nitrogen container (a vacuum bottle plugged with a silicone-rubber stopper fixed with screw clamps); 6 = liquid-nitrogen carrier tube (ca. 600 mm × 2 mm I.D. × 3.2 mm O.D. PTFE tube); 7 = GC control microprocessor; 8 = temperature monitor; 9 = fine sheath thermocouple; 10 = screw clasp; 11 = mist feeder (125 mm × 4.5 mm I.D. × 6.4 mm O.D. SUS316 stainless-steel end-stopped tube); 12 = connection tube (150 mm × 2.0 mm I.D. × 3.2 mm O.D. SUS 316 stainless-steel open tube); 13 = cold trap (a 100 mm × 3.2 mm I.D. × 4.0 mm O.D. PTFE open tube); 14 = 0.5–0.7 mm diameter pin-hole; 15 = cryofocusing tube.

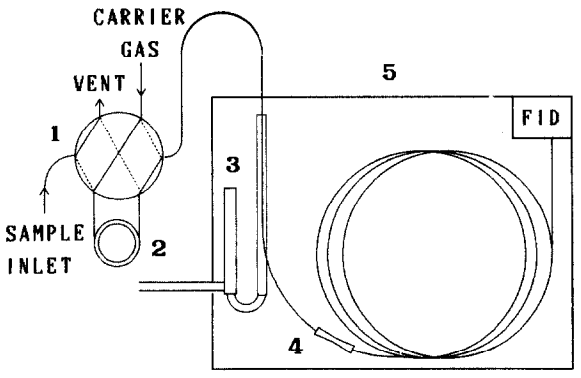

Fig. 2. Analytical system. 1 = Sampling valve; 2 = 1-, 2- or 9-ml sampling loop; 3 = cryofocusing system; 4 = glass seal connector; 5 = gas chromatograph with detector.

open-tubular (OVWOT) column or (2) a 30 m × 0.25 mm I.D. OV-1 capillary (OVC) column (Ohio Valley, Marietta, OH, USA) and a flame ionization detector. For the former column, the temperature was 30°C for 1 min, then programmed at 5°C/min to 100°C (250°C for the analysis of industrial emissions), and the carrier was 4.5 ml/min of nitrogen. For the latter column, the temperature was 30°C for 2.2 min, then programmed at 5°C to 100°C (250°C for the analysis of industrial emissions), and the carrier was 1.0 ml/min of nitrogen. The detector temperature was 250°C.

For the determination of sulphur compounds, a Varian (Walnut Creek, CA, USA) Model 1440 gas chromatograph was equipped with a 30 m × 0.53 mm I.D. OVWOT column and a flame photometric detector. The column temperature was 30°C for 3 min, then programmed at 5°C/min to 100°C, the carrier was 4.5 ml/min of nitrogen and the detector temperature was 160°C.

Analytical procedure

The cold trap was cooled to −165°C. A 1-, 2- or 9-ml volume of an air sample was taken in a sampling loop and transported into the cold trap with a carrier volume more than double the sample volume. Cooling was stopped and GC analysis was started. The components were identified by their retention times and determined from their peak areas.

RESULTS AND DISCUSSION

Cryostat system

The configuration of the proposed trap was effective in avoiding gradient cooling of the cryofocusing tube due to coarse cryogen droplets and did not affect the GC oven temperature. Fig. 3 shows temperature-control aspects at the cold trap. The trap temperature reached the desired temperature (−65 to −165°C) within 2 min after the start of the cooling. The temperature recovered to the oven temperature (30°C) within 2 min after stopping the cooling. A temperature dip was observed at the trap soon after the start of cooling, owing to heat conductance across the wall of the liquid-nitrogen carrier tube. This dip had no adverse effects on the analysis.

The temperature of the cooling zone depended strictly on the flow-rate of liquid nitrogen driven to the trap. The internal pressure of the liquid-oxygen container was differentially controlled by introducing 2.5–5.0 p.s.i. of nitrogen gas (determined considering the GC oven temperature and the trap temperature) into the container and by releasing the nitrogen from the container at a limited rate from valve B under the command of the temperature monitor. As a result, the temperature was precisely controlled down to −165°C. The temperature monitor indicated −165 ± ⩽2°C when it was set to −165°C. The cold trap could also be cooled to below −165°C. However, coarse cryogen droplets appeared on the thermocouple and disturbed the temperature monitor. Precise temperature control became more difficult at lower temperatures.

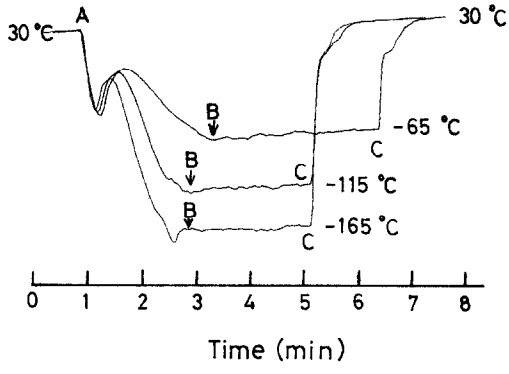

Fig. 3. Temperature-control aspects at the cold trap. (A) Cooling "on"; (B) sample introduction; (C) cooling "off".

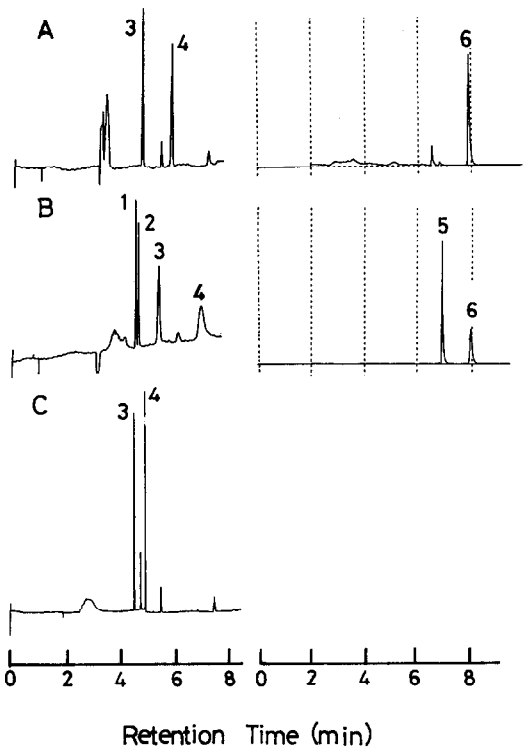

Fig. 4. Chromatograms of low-boiling compounds. Sample volume: 1 and 9 ml for analysis of hydrocarbons and sulphur compounds, respectively. For A, B and C, see Table I. Peaks: 1 = ethane (1 ppm); 2 = ethylene (1 ppm); 3 = propane (1 ppm); 4 = butane (1 ppm); 5 = hydrogen sulphide (0.8 ppm); 6 = methanethiol (0.5 ppm).

The cold trap and the carrier tube were of low heat capacity. Only the necessary amount of the cryogen was directed to the trap from the container. As a result, consumption of the cryogen was minimized. The trap had no effect on the GC oven temperature. A 180-ml volume of liquid nitrogen was consumed in a single run, requiring cooling for 5 min at −165°C. This is a very low consumption of the cryogen compared with conventional techniques.

The cryosat system was automatically operated by the microprocessor, using the low-pressure driving gas without direct handling of the cryogen during the analysis. The system was therefore safe in use.

Introduction of low-boiling compounds into a capillary column

The cryofocusing effects and the analytical accuracy were investigated by using gas samples containing 0.5–1.0 ppm (v/v) of low-boiling compounds such as C_1–C_4 aliphatic hydrocarbons, hydrogen sulphide and methanethiol. Fig. 4 shows chromatograms of these compounds and Table I indicates the analytical accuracy. The PLOT column was effective for cryofocusing the low-boiling compounds except methane. Ethane, ethylene and higher boiling hydrocarbons were well trapped in the cryofocusing tube at −165°C and accurately de-

TABLE I

ANALYTICAL ACCURACY FOR LOW-BOILING COMPOUNDS

S.D. = standard deviation; R.S.D. = relative standard deviation; n.d. = not detectable.

Compound[a]	Parameter[b]	A[c]	B[c]	C[c]
Ethane	S	n.d.	10.0 ± 0.07 (0.7)	n.d.
	PW	–	0.030 ± 0.0008	–
Ethylene	S	n.d.	10.1 ± 0.11 (1.1)	n.d.
	PW	–	0.026 ± 0.0009	–
Propane	S	15.8 ± 0.28 (1.8)	15.0 ± 0.17 (1.3)	15.7 ± 0.42 (2.7)
	PW	0.040 ± 0.0014	0.084 ± 0.0084	0.017 ± 0.013
Butane	S	18.0 ± 0.20 (1.1)	14.0 ± 0.096 (6.9)	17.9 ± 0.48 (2.7)
	PW	0.061 ± 0.0023	0.326 ± 0.0178	0.016 ± 0.0005
Hydrogen sulphide	S	n.d.	55.1 ± 4.20 (7.6)	n.d.
	PW	–	0.044 ± 0.0055	–
Methanethiol	S	33.7 ± 1.23 (3.6)	28.8 ± 1.50 (5.2)	n.d.
	PW	0.068 ± 0.0045	0.092 ± 0.0084	–

[a] Concentrations of ethane, ethylene, propane and butane = 1 ppm (v/v), hydrogen sulphide = 0.8 ppm and methanethiol = 0.5 ppm.
[b] S = Signal output of area ± S.D. (R.S.D., %) (average of five runs); PW = peak width ± S.D. (min) (average of five runs).
[c] Combination of a cryofocusing tube and an analytical column; (A) FST and OVWOTC; (B) PLOTC and OVWOTC; (C) FST and OVCC. Sample volume: 1 and 9 ml for hydrocarbons and sulphur compounds, respectively. For GC conditions, see text.

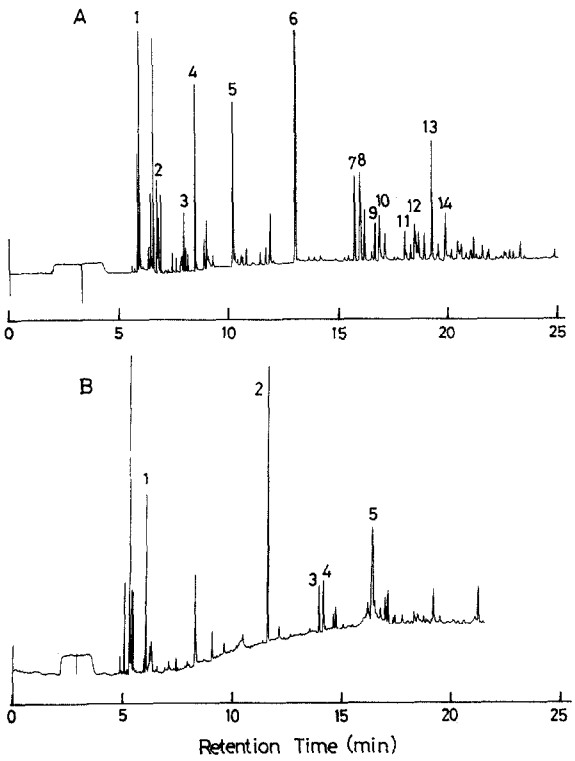

Fig. 5. Analyses of ambient air samples polluted by industrial emissions. For analytical conditions, see text. (A) Emission gas from a steel baking–coating process. Sample volume, 2 ml. Peaks: 1 = propionaldehyde (301 ppb, v/v); 2 = isopropanol (80 ppb); 3 = butyraldehyde (34 ppb); 4 = ethyl acetate (140 ppb); 5 = *n*-butanol (280 ppb); 6 = toluene (430 ppb); 7 = ethylbenzene (71 ppb); 8 = *m,p*-xylene (92 ppb); 9 = *o*-xylene (30 ppb); 10 = butyl Cellosove (79 ppb); 11 = benzaldehyde (32 ppb); 12 = *m*-ethyltoluene (32 ppb); 13 = pseudocumene (80 ppb); 14 = hemimellitene (43 ppb). (B) Emission gas from a photogravure printing works. Sample volume, 2 ml. Peaks: 1 = 2-propanol (15 ppb); 2 = toluene (56 ppb); 3 = ethylbenzene (14 ppb); 4 = *m,p*-xylene (19 ppb); 5 = *o*-xylene (7.4 ppb). All values (ppb) in American billion (10^9).

termined by GC with the OVWOT column. The detection limits of the hydrocarbons were 19–30 pg at three times the signal-to-noise ratio. Hydrogen sulphide and methanethiol were also well determined. The higher boiling organics were also effectively trapped on an ordinary fused-silica column. A higher trap temperature could therefore be selected for the determination of higher boiling organics to save the cryogen.

Application to analysis of environmental gas samples

Ambient air samples polluted by industrial emission sources were analysed by using the system with a 2-ml sampling loop (see Fig. 2) for hydrocarbons, aldehydes and others. Fig. 5 shows chromatograms for the succesful analysis of polluted air samples. Sharp and highly-resolved peaks were obtained for lower boiling compounds compared with conventional analysis.

CONCLUSIONS

The proposed cryofocusing system is convenient and useful for introducing low-boiling compounds except methane into a capillary column. The temperature of the 10-cm cryofocusing segment is accurately controlled at any desired temperature down to −165°C. Automatic operation can be programmed using a GC control microprocessor or other controller together with the GC operating parameters. The cryofocusing kit is easy to instal in any GC system. Operation is safe as there is no direct handling of the cryogen. The system may be useful for the determination of volatile organics in industrial emissions and air samples.

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