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GAS CHROMATOGRAPHIC DETERMINATION OF TRACE AMOUNTS OF HYDROCARBONS IN THE ATMOSPHERE OF EXPERIMENTAL BIOLOGICAL CONTAINERS

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SUMMARY

A method has been developed for the gas chromatographic determination of hydrocarbons in concentrations down to 1–10 ppb in the atmosphere of experimental biological containers (gaseous exhalations of dormant and budding potatoes, leaf tissue, germinating seeds, etc.) having a free volume of 1500 ml. A two-step pre-concentration on Porapak Q at −78° is employed. After the first concentration step, the gases are desorbed at 150° and are transported to the second pre-concentration step and thence to the hydrogen carrier-gas stream and the gas chromatograph. Water and carbon dioxide are eliminated on finely granulated sodium hydroxide.

INTRODUCTION

In the gas chromatographic (GC) determination of hydrocarbons in urban and industrial atmospheres the hydrocarbons are pre-concentrated by condensation at the temperature of liquid air[1,2] or by adsorption on active charcoal[3], silica[4,5], di-*n*-butyl phthalate on a Sil-O-Cel support[6], alumina[3], etc., at the temperature of liquid air or solid carbon dioxide. Interference from atmospheric humidity is eliminated by introduction of a desiccating tube containing phosphorus pentoxide or magnesium perchlorate, and oxygen, nitrogen and hydrogen are removed at the temperature of liquid air[1].

Ethylene, the simplest plant hormone and a general product of plant tissues[7], and other hydrocarbons have been the subject of intense study from the point of view of their interactions with other growth substances. Only rarely is ethylene liberated from plant tissues in an amount sufficient for direct determination[8]; pre-concentration and flame-ionization detection are generally necessary. In this way, ethylene has been

determined in plant tissues[9] and, together with other hydrocarbons, in the atmosphere of experimental containers[10].

The purpose of our experiments was to develop a precise and sensitive method for the determination of trace amounts of hydrocarbons, which could be applied in research and industrial laboratories and which did not require complex apparatus and procedure. The method chosen employs two-step pre-concentration on Porapak Q at −78°.

EXPERIMENTAL

The determination was carried out on a Giede GCHF 18.3 gas chromatograph equipped with a flame-ionization detector (FID). Porapak Q (Waters Assoc., Milford, Mass., U.S.A.; 50–80 mesh, batch No. 816) was used both for pre-concentration and as the packing material for the chromatographic column.

The first pre-concentration step was carried out in a closed circuit (Fig. 1) containing a Chemoprojekt MP No. 873 membrane pump (1) whose outlet was connected to a flow-meter (2) and from which the air was led through a stoppered tube into a vacuum desiccator (3). The air was pumped from the desiccator through a tube placed above the plate containing the plant material and into a stainless-steel U-tube (30 cm × 0.4 cm) (4) packed with 1.1 g of Porapak Q. The packing was supported by two layers of quartz wool. The U-tube was cooled to −78° by a mixture of solid CO_2 and methanol in a Dewar flask. The outlet of the U-tube was connected to the inlet of the membrane pump, thus closing the circuit. The desiccator was purged four times within 10 min at an air flow-rate of 420 ml/min; the desiccator free volume was 1000–1050 ml. During this procedure, not only hydrocarbons but also carbon dioxide and water are concentrated in the U-tube.

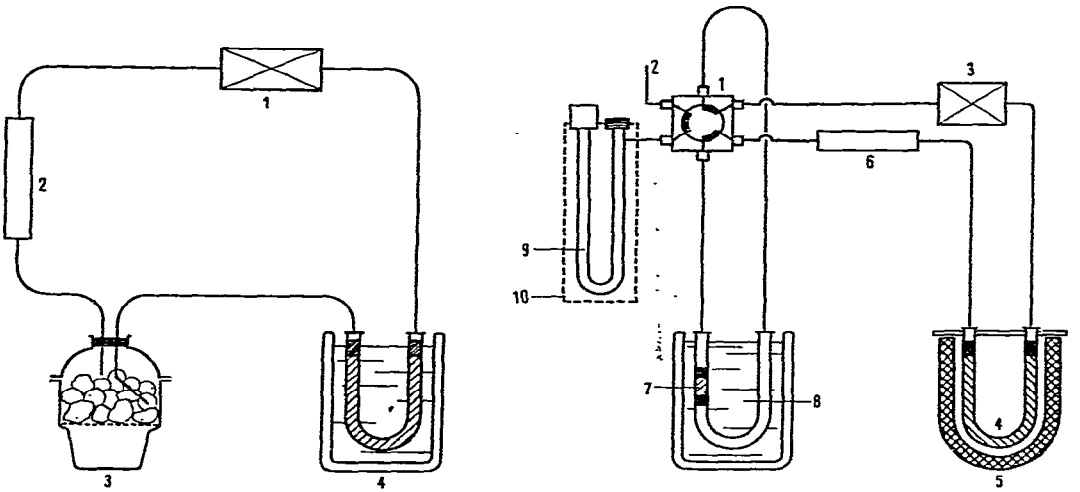


Fig. 1. Scheme of the first gas pre-concentration step: 1 = membrane pump; 2 = flow-meter; 3 = biological container; 4 = U-tube in the cooling bath.

Fig. 2. Scheme of the second gas pre-concentration step: 1 = six-way valve; 2 = carrier-gas inlet; 3 = membrane pump; 4 = U-tube; 5 = heating mantle; 6 = sodium hydroxide tube; 7 = glass capillary; 8 = cooling bath; 9 = chromatographic column; 10 = thermostat.

In the following operation the pre-concentrated gases were transferred to a 40–50 times smaller amount of Porapak Q (Fig. 2). The membrane pump (3) outlet was connected to the U-tube (4) packed with Porapak Q in which the gases were concentrated in the previous operation. The U-tube was placed in a heating mantle (5) and heated to 150°. The U-tube outlet was connected to a tube (17.0 cm × 1.5 cm) (6) packed with 16 g of finely granulated sodium hydroxide between two layers of quartz wool. The tube (6) was connected to a six-way valve (1) through which the gases were led into a U-shaped glass capillary (40 cm × 0.15 cm) (7). The capillary narrowed to an internal diameter of 0.1–0.08 cm over a length of 2 cm in the inlet arm. In this narrow part were packed 0.025 g of Porapak Q, between two layers of quartz wool. The capillary was cooled to −78° in a Dewar vessel (8). The capillary outlet was connected to inlet of the membrane pump (3) by means of a six-way valve. The time required for transfer to the second pre-concentration step was 5 min. The membrane pump was then switched off, and the capillary was removed from the cooling bath, dried and tempered in the air and placed in a heating mantle. As soon as the capillary had attained 150°, the six-way valve (1) was turned, thus transferring the desorbed gases into the hydrogen carrier-gas flow (2) by which they are transported into the GC column (9) in the thermostat (10).

A spiral chromatographic column (100 cm × 0.4 cm) packed with Porapak Q was employed for the separation. The measurements were carried out at a thermostat temperature of 60° and at a flow-rate and pressure of hydrogen carrier gas of 24.2 ml/min and 30.4 kPa, respectively.

The ethylene used (ČSSR Chemical Works, Záluží in Krušné Hory, Czechoslovakia) had the composition (in vol. %): N_2, 0.6; O_2, 0.08; CO_2, 0.09 and C_2H_6, 0.6. Propylene from the same supplier contained the following impurities (in vol. %): N_2, 0.03; O_2, 0.01; CH_4, 1.63; C_2H_4, 0.008 and C_2H_6, 0.052. Ethane was prepared by hydrogenation of ethylene on a Ni–ThO_2 catalyst, as described earlier[8].

Gaseous samples were injected by means of a Hamilton Type 1705N syringe (Clark Hamilton Manufacturing, Switzerland) and a Record (2 cm^3) Model 397 161-301 medical hypodermic syringe (Chirana, Stará Turá, Czechoslovakia).

RESULTS AND DISCUSSION

Selection of a suitable adsorbent

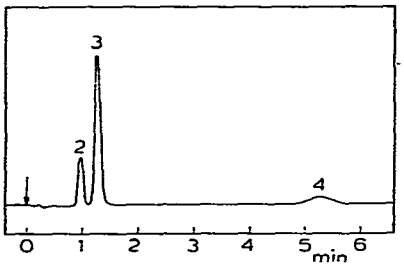
Our choice of adsorbent was based on the experience of previous workers[1–6], and the substances recommended by them, especially silica, were tested. We found that Porapak Q, which we proposed earlier and which is characterized by a high surface area, stability of the elution data, inertness toward polar compounds and stability at both high and low temperatures, is more suitable than the materials previously used.

The specific retention volumes for ethylene in hydrogen and nitrogen, 7100 and 5252 ml, respectively, were determined at the temperature of the cooling bath used, *i.e.*, −78°. It follows from these data that 1 g of Porapak Q is sufficient for quantitative adsorption of ethylene and higher hydrocarbons from a volume of 1500 ml during the first pre-concentration step. On the other hand, the gases are very rapidly desorbed on heating to 150°, which is advantageous for the transfer to the second pre-concentration step and for injection of the concentrate into the chromatographic

column. Water, which is a constant component of the atmosphere of experimental vessels containing plant materials, is eluted after the first pre-concentration step immediately after ethane and is retained on the finely granulated NaOH, together with carbon dioxide; it is not transferred to the second pre-concentration step and does not interfere with the injection and detection processes.

Comparison of the results of the analysis of a model mixture after direct injection and after pre-concentration

A model mixture of ethylene (130 ppm), ethane (287.5 ppm) and propylene (125 ppm) in hydrogen was prepared. 2 ml of the mixture was injected directly into the gas chromatograph and a chromatogram was obtained (Fig. 3) the evaluation of which gave: ethylene, 0.26 μl; ethane, 0.575 μl; propylene, 0.25 μl. 2 ml of the model mixture were then transferred in a syringe to a gas burette filled with nitrogen, thus yielding a mixture consisting of 0.52 ppm of ethylene, 1.16 ppm of ethane and 0.50 ppm of propylene. After pre-concentration, 0.26 μl of ethylene, 0.58 μl of ethane and 0.32 μl of propylene were found (Fig. 4). A calibration mixture was prepared accord-



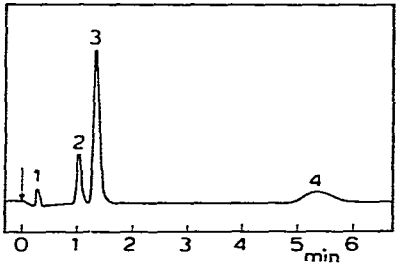


Fig. 3. Chromatogram obtained on direct injection of 2 ml of a model mixture of 130 ppm of ethylene (2), 287.5 ppm of ethane (3) and 125 ppm of propylene (4).

Fig. 4. Chromatogram of a model mixture of the same total amounts of gases as in Fig. 3 but diluted to 0.52 ppm of ethylene (2), 1.16 ppm of ethane (3) and 0.50 ppm of propylene (4) and then pre-concentrated.

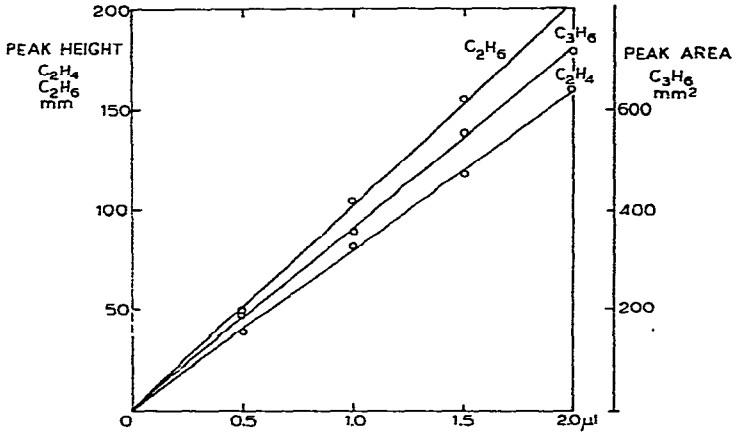


Fig. 5. Calibration graph obtained for an ethylene–ethane–propylene mixture after two-step pre-concentration (amplifier input resistance, $10^9\ \Omega$; sensitivity, $\times 30$).

ing to Novák[11], and the calibration graph for the mixture of ethylene, ethane and propylene is given in Fig. 5.

Analysis of the atmospheres in biological containers

The liberation of hydrocarbons by stored potatoes was studied; after pre-concentration using the above procedure, the chromatogram in Fig. 6 was obtained (for germinating potatoes of the Sperber variety, weight 1010 g; desiccator free volume, 1050 ml; temperature of dark thermostat, 17°; relative atmospheric humidity, 70%; amplifier input resistance, $10^9\ \Omega$; sensitivity, × 10). When the temperature of the gas chromatograph thermostat was 60°, the individual components of the atmosphere were satisfactorily separated and were identified as air, methane, ethylene (0.10 ppm), ethane (0.30 ppm), and propylene (0.21 ppm).

In an analysis of the atmosphere surrounding dormant potatoes of the Jiskra variety (weight, 1040 g; desiccator free volume, 1350 ml; air temperature, 5°; relative atmospheric humidity, 85%; amplifier input resistance, $10^{10}\ \Omega$; sensitivity, × 100) the chromatogram in Fig. 7 was obtained when the temperature of the gas chromatograph thermostat was 60°. The components of the atmosphere were identified as air, methane, ethylene (1.2 ppb), ethane (2.5 ppb) and propylene (8 ppb).

Determination of the accuracy of the method

Ten determinations of ethylene, ethane and propylene were carried out for three model mixtures having the compositions: ethylene, 1.03–3.5 ppm; ethane, 0.65–2.68 ppm; propylene, 0.90–1.79 ppm. All of the mixtures were prepared in a 500-ml gas burette and pre-concentrated using the above method. The relative con-

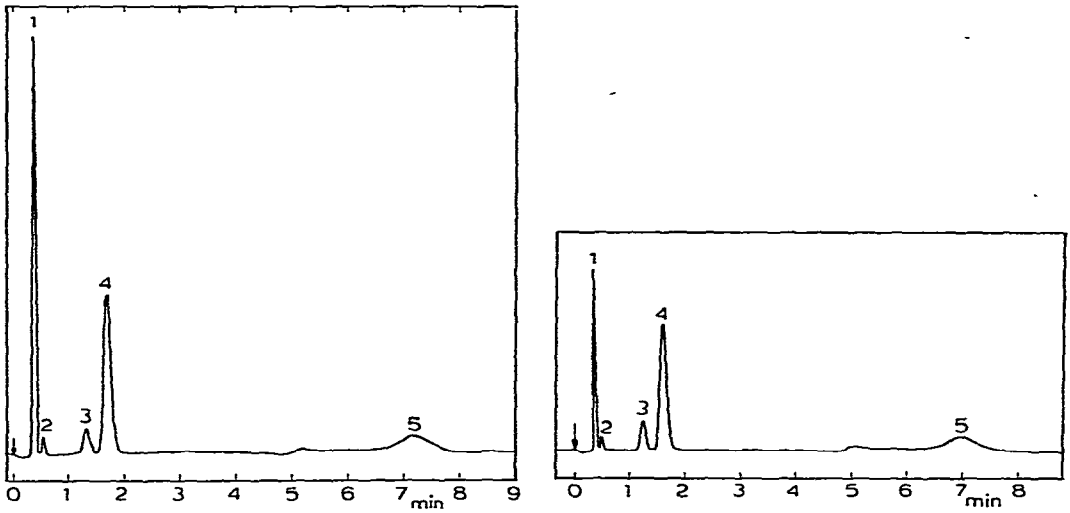


Fig. 6. Chromatogram obtained after pre-concentration of the atmosphere from an experimental vessel containing budding potatoes of the Sperber variety. Peaks: 1 = air; 2 = methane; 3 = ethylene; 4 = ethane; 5 = propylene.

Fig. 7. Chromatogram obtained after pre-concentration of the atmosphere from an experimental vessel containing potatoes of the Jiskra variety at the end of the endogenous dormancy period. Peaks as in Fig. 6.

fidence limits for these three mixtures were determined as: $\tau = 2.74$, 4.46 and 7.73% for ethylene; $\tau = 2.41$, 3.36 and 5.53% for ethane and $\tau = 4.38$, 6.16 and 9.97% for propylene.

Comparison of our results with previous work[3], which gave pre-concentration efficiency values of 75.8% for silica and 81.8% for active charcoal, indicates that the proposed method is sufficiently precise. Comparison with the results obtained by Feldstein and Balestrieri[2], who reported an efficiency of 95–100% for pre-concentration of 150 ml of a gaseous sample using a freezing-out loop cooled with liquid air, is also noteworthy.

CONCLUSIONS

A method has been developed for the gas chromatographic determination of minute amounts of hydrocarbons in the atmosphere of biological containers. A two-step pre-concentration on Porapak Q is employed at a temperature of −78°. The resulting chromatograms of hydrocarbons from vessels of free volume 1500 ml contain.ig budding potatoes consisted of three well-resolved peaks corresponding to ethylene, ethane and propylene. The time required for the whole procedure was 25 min. The method is capable of detecting 1 ppb of ethylene and ethane and 10 ppb of propylene in the given volume.

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