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Note

Simultaneous gas chromatographic separation of volatile organic sulphur compounds and C_1–C_4 hydrocarbons

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In the course of investigations on the formation of volatile biochemical precursor compounds in methane–hydrogen sulphide atmospheres[1], it appeared necessary to carry out an extensive gas chromatographic separation of volatile C_1–C_4 hydrocarbons and organic sulphur-containing compounds.

Several types of supports and liquid phases have already been used for the gas chromatographic separation of organic sulphur compounds, especially for the homologous series of aliphatic thiols and sulphides. These studies were reviewed recently[2,3]. Some of the previously reported analyses include the results of only a few low-molecular-weight sulphur compounds[4–9]. In addition, the C_1–C_4 hydrocarbons may interfere in the separation[7], and even when there is no interference between volatile organic sulphur compounds and C_1–C_4 hydrocarbons, the separation of the hydrocarbons is poor[10,11].

This paper describes the simultaneous separation of volatile sulphur compounds and C_1–C_4 hydrocarbons on a Durapak OPN–Porasil C column, with an exhaustive calibration of this column for the C_1–C_4 alkanethiols and the C_1–C_4 alkyl sulphides. The relative molar responses to the flame ionization detector of the tested sulphur compounds relative to ethanethiol are presented.

EXPERIMENTAL

Apparatus

The chromatograph was a Varian Aerograph Model 1520 equipped with flame ionization detectors and a linear temperature programmer. An Autolab Model 6300 digital integrator was used for determining the peak areas.

Reagents

All the hydrocarbons were purchased from l'Air Liquide S.A. (Le Plessis-Robinson, France), 1,3-propanedithiol from Aldrich (Milwaukee, Wisc., U.S.A.), 1,2-ethanedithiol from J. T. Baker (Deventer, The Netherlands), diethyl disulphide from K & K Labs. (Plainview, N.Y., U.S.A.) and thiophene from Prolabo (Paris, France).

Methanethiol, 1-propanethiol, 2-propanethiol, 2-methyl-2-propanethiol, 1-butanethiol, 2-butanethiol, 1,2-propanedithiol, 1,4-butanedithiol, methyl ethyl sulphide, 1,2-epithiopropane (propylene sulphide) and tetrahydrothiophene were Fluka (Buchs, Switzerland) products.

2-Propene-1-thiol, 2-methyl-1-propanethiol, 2-methyl-2-propene-1-thiol, methyl isopropyl sulphide, methyl *n*-propyl sulphide, thiirane (methylene sulphide) and thiacyclobutane (trimethylene sulphide) were purchased from Pfaltz and Bauer (Flushing, N.Y., U.S.A.), and ethanethiol, dimethyl sulphide and diethyl sulphide from Schuchardt (Munich, G.F.R.).

Chromatography

The chromatographic column was a 2 m long, 1.5 mm I.D. PTFE tube packed with Durapak OPN–Porasil C, 80–100 mesh (Waters Ass., Framingham, Mass., U.S.A.). The Durapak packing is impregnated with the liquid phase (OPN, *i.e.* β,β'-oxidipropionitrile), chemically bonded to the siliceous support (Porasil C).

The temperature programme was: isothermal at 20° for 6 min, then increased at 2°/min to a final temperature of 130°, held for 10 min; the temperature of the injector was 200° and that of the detector (FID) was 210°C. The flow-rates employed were: carrier gas (nitrogen), 25 ml/min; hydrogen, 30 ml/min; and air, 300 ml/min.

RESULTS AND DISCUSSION

Fig. 1a shows a chromatogram for a sample containing C_1–C_4 hydrocarbons. A good separation of these hydrocarbons is obtained within 5 min, during the 20° isothermal step of the temperature programme. Nevertheless, ethane and ethylene, and isobutene and *trans*-butene-2, are co-eluted.

Fig. 1b represents the gas chromatographic analysis of virtually all of the volatile organic sulphur compounds that contain 1–4 carbon atoms. They are all eluted after the isothermal step of the temperature programme, so their separation does not interfere in the separation of the C_1–C_4 hydrocarbons. All of the alkanethiols and alkyl sulphides and most of the unsaturated thiols and sulphur heterocyclics containing 1–4 carbon atoms were present in the sample. In addition, some sulphur compounds with higher boiling points, including dithiols and disulphides, were also injected for comparison and extensive calibration of the column. There is no separation between ethyl methyl sulphide and 2-butanethiol, and 2-methyl-1-propanethiol and 2-methyl-2-propene-1-thiol, but all of the other sulphur compounds can be distinguished.

A quantitative study of the gas–liquid chromatography of these compounds was performed by determining the relative molar response (*RMR*) of each sulphur compound with respect to ethanethiol. The *RMR* values are given in Table I for each sulphur compound, according to structural groups present; boiling points and retention temperatures are also presented.

Theoretically, this list of volatile organic C_1–C_4 sulphur compounds is not exhaustive. From the behaviour observed on the Durapak column of the different homologous series of sulphur compounds examined, it is possible to determine approximately the retention temperatures of the missing compounds. Hence the calibration of the column can be considered to be exhaustive for sulphur compounds with retention temperatures up to 80°.

Classical qualitative analysis in gas chromatography is based on the comparison between retention times of known and unknown compounds. However, even with simultaneous injection of standards with the sample to be analyzed,

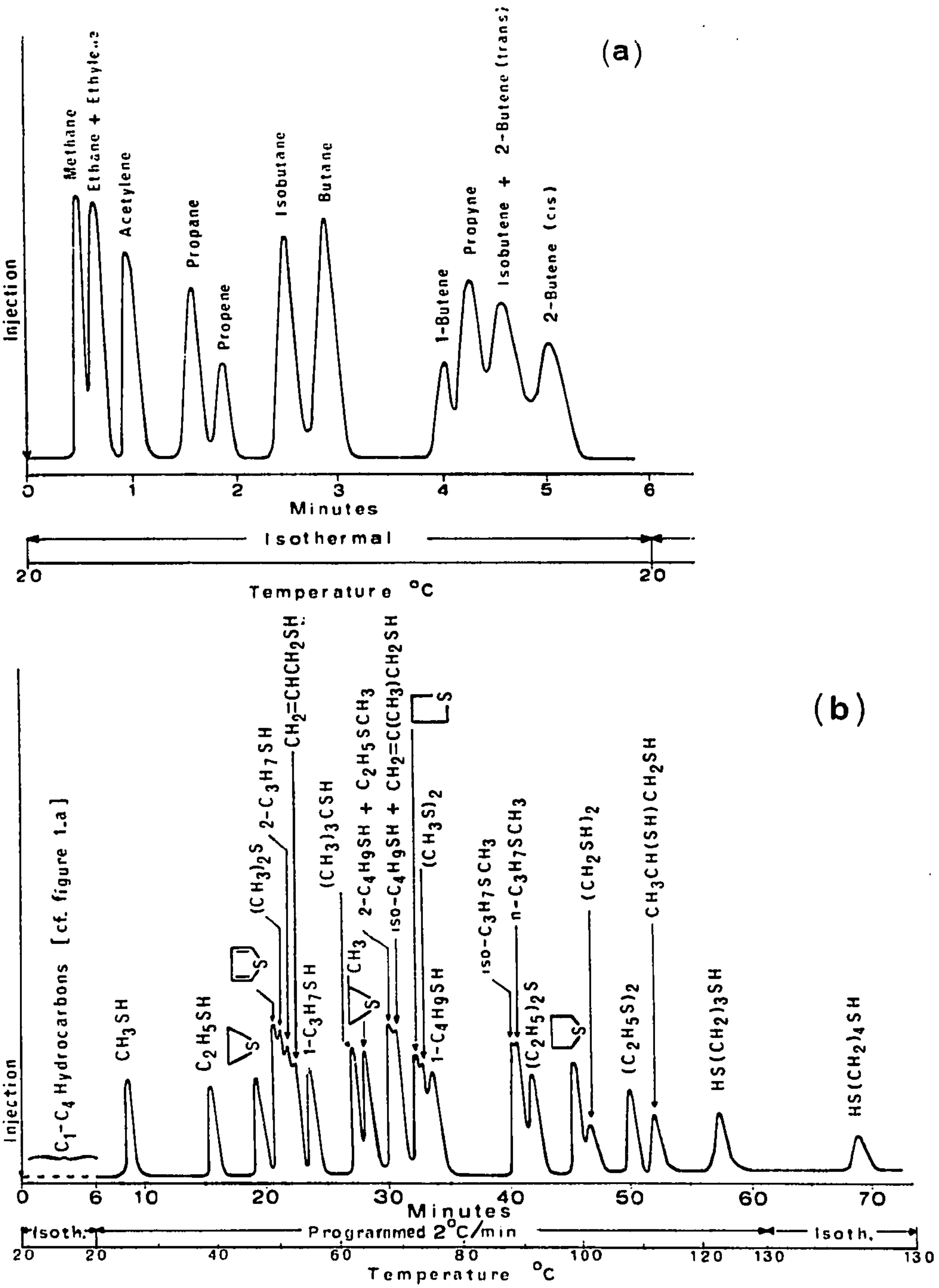

Fig. 1. (a) GLC of a C_1–C_4 hydrocarbons mixture. (b) GLC of 26 sulphur compounds. Amount injected: about 5 μg of each compound. Column: Durapak OPN–Porasil C, 80–100 mesh, 2 m × 1.5 mm I.D., PTFE. Conditions: injector, 200°; detector, 210°; initial temperature, 20°, 6 min initial hold, then 2°/min to 130°; carrier gas, nitrogen at a flow-rate of 25 ml/min. Sensitivity: $5 \cdot 10^{-9}$ A full-scale.

TABLE I

RELATIVE MOLAR RESPONSES, BOILING POINTS AND RETENTION TEMPERATURES OF C_1–C_4 SULPHUR COMPOUNDS

Sulphur compound	*RMR*, sulphur compound/EtSH*	*B.p. (°C)*	*Retention temperature (°C)*
Alkanethiols			
Methanethiol	0.56	6	25.3
Ethanethiol	1.00	33–36	39.0
2-Propanethiol	1.59	57–60	51.7
1-Propanethiol	1.55	66–68	55.3
2-Methyl-2 propanethiol	2.07	62–67	62.7
2-Butanethiol	1.93	85	68.3
2-Methyl-1-propanethiol	1.80	88	69.7
1-Butanethiol	1.84	96–98	75.7
Alkenethiols			
2-Propene-1-thiol	0.67	67–68	53.0
2-Methyl-2-propene-1-thiol	0.46**	90–95	69.7
Dithiols			
1,2-Ethanedithiol	0.86	146	102
1,2-Propanedithiol	1.08	150–160	112
1,3-Propanedithiol	1.48	173	123
1,4-Butanedithiol	1.12**	195–196	130
Sulphides			
Dimethyl sulphide	1.00	37	50.7
Methyl ethyl sulphide	1.40	66	68.3
Methyl isopropyl sulphide	1.70	85	88.7
Methyl *n*-propyl sulphide	2.07	95–96	89.3
Diethyl sulphide	2.21	92	92.0
Disulphides			
Dimethyl disulphide	0.91	116–118	74
Diethyl disulphide	1.80	153	108
Heterocyclics			
Thiirane	0.99	55–56	46.7
1,2-Epithiopropane	1.52	72–75	64.7
Thiophene	2.39	84	49.3
Thiacyclobutane	1.58	94	72.7
Tetrahydrothiophene	2.17	119	99.0

* Average of three independent analyses; ethanethiol as reference.

** Non-quantitative elution.

there is the risk of incorrect assignment of the identity of peaks, owing to coincidence of the retention values of several compounds at a particular position on the chromatogram. Nevertheless, if the peaks to be identified are located in the area where exhaustive gas chromatographic calibration has been carried out, the identification can be achieved with certainty.

The exhaustive calibration of the Durapak OPN–Porasil C column for retention temperatures up to 80° has been used successfully in our laboratory for qualitative and quantitative analyses of gaseous samples containing C_1–C_4 hydrocarbons and volatile organic sulphur compounds[1].

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