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Short Communication

Determination of volatile thiols by gas chromatography using separation as tributyltin mercaptides

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ABSTRACT

Thiols were converted with a 0.01 *M* solution of tributyltin hydroxide in hexane to tributyltin mercaptides. Part of the hexane solution was evaporated in a small test tube on a water bath, hexane vapour was removed and the remaining mercaptides were decomposed with 3 *M* hydrochloric acid saturated with ammonium sulphate. A sample of 1.2 ml from the total headspace of 1.3 ml was applied on the column of a gas chromatograph using nitrogen gas and flame ionization defection. The average relative standard deviation of the peak height for 10 nmol of each of seven different thiols was 11%. The method is illustrated by analysis of thiols separated from cigarette smoke.

INTRODUCTION

In the course of investigation of sulphur compounds in the environment it became apparent that it was necessary to develop a reliable analytical method for volatile thiols in air, smoke, water, food, soil and biological materials. The resolution of thiols by gas–liquid chromatography is well established [1], but the isolation is difficult to perform or not at all suitable for trace amounts. The thiols can be isolated from the gas phase as mercury [2,3], cadmium [3] and mercuribenzoic acid [4] mercaptides. The disadvantage of these reagents however is that the precipitates are troublesome to deal with and they easily deompose into metal sulphide and thioether.

Although flame photometric detection combined with gas chromatography has been found to be very valuable for the determination of a few sulphur compounds in air [5], the results for complex mixtures cannot be regarded as satisfactory. The analysis of sulphur compounds in tobacco smoke is virtually limited to carbon disulphide, carbonyl sulphide, hydrogen sulphide, sulphur dioxide, dimethylsulphide, dimethyldisulphide, diethylsulphide and thiophene [6–8]. About 30 peaks remain unknown, and no results concerning the thiol composition have been reported.

Another approach to gas chromatographic analysis of thiols is based on deri-

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vatization either to pentafluorobenzyl ethers [9] or to dinitrophenylalkyl thioethers [10].

The method suggested in this paper involves conversion of thiols to tributyltin mercaptides dissolved in hexane, evaporation of hexane with other volatile compounds, if any, decomposition with hydrochloric acid and application of the gas from the headspace to the chromatograph. By this approach the thiols are completely separated from other volatile compounds, apart from hydrogen sulphide, which however does not interfere when flame ionization detection is used.

EXPERIMENTAL

A Chrom 4 gas chromatograph (Laboratorni Přistroje, Prague, Czechoslovakia) equipped with a flame ionization detector and a glass column (2.5 m × 3 mm I.D.) packed with 5% tricresylphosphate on Chromosorb G AW 60–80 mesh was used. The column was operated at 37°C with a nitrogen carrier gas flow-rate of 16 ml/min, a hydrogen flow-rate of 25 ml/min and an air flow-rate of 300 ml/min. The sensitivity was 1:1 (full sensitivity), and the detector response 5 mV = 25 cm.

To prepare a stock solution of *o*-hydroxymercuribenzoic acid (HMB), dissolve 0.321 g of *o*-hydroxymercuribenzoic acid anhydride in 10 ml of 2 *M* potassium hydroxide and dilute to 200 ml with water. To 10 ml of the stock solution ($5 \cdot 10^{-3}$ *M*) add 1 ml of dibutylamine and dilute with methanol to 500 ml, the concentration being 10^{-4} *M*.

To prepare a stock solution of tributyltin (TBT) hydroxide, dissolve 3 ml of tributyltin chloride in 100 ml of hexane and shake for 5 min with 25 ml of 2 *M* potassium hydroxide. Leave aside overnight, remove the aqueous phase and filter through paper. To obtain 0.01 *M* TBT hydroxide, dilute the stock solution with hexane in a ratio of 1:10.

The prepared solutions of thiols in hexane were analysed by titration with HMB (sample + a few millilitres of *n*-propanol + 0.5 ml of 2 *M* potassium hydroxide, dithizone as indicator) and diluted to obtain 10^{-5}–10^{-4} *M* concentrations in 0.01*M* TBT in hexane.

Separation of thiols from aqueous samples

To 100 ml of the sample add 0.5 ml of 2 *M* potassium hydroxide, 2 g of sodium sulphite and 1 ml of 0.1 *M* Na_2EDTA and shake for 2 min with 5 ml of 0.01 *M* TBT in hexane. To reduce vaporization of hexane cool the sample to 5°C. Use the hexane phase for analysis.

Separation of thiols from water-miscible solvents

Shake together 5 ml of the sample, 5 ml of 0.01 *M* TBT in hexane and 10 ml of a 4% aqueous solution of ammonium sulphate; separate the hexane phase and wash it with water and with 0.1 *M* potassium hydroxide.

Separation of thiols from gases

The thiols are absorbed in a small gas-washing bottle containing 5 ml of 0.01 *M* TBT in hexane and 5 ml of 0.1 *M* potassium hydroxide and cooled with iced water.

Thiols are always separated with hydrogen sulphide and the total concentration can be determined by titration with HMB.

TABLE I

DETERMINATION OF THIOLS BY GAS CHROMATOGRAPHY AND HEADSPACE METHOD

Thiol	Amount taken (nmol)						Relative peak area with regard to methanethiol	Retention time (min)	Average peak height per nmol (mm)
	5	10	15	5	10	15			
	Average peak height (mm)			Relative standard deviation for $n = 5$ (%)					
Methanethiol	15	33	48	21	7	8	1.0	2.4	3.2 ± 0.2
Ethanethiol	27	60	95	14	4	4	3.1	4.0	5.9 ± 0.5
2-Propanethiol	43	89	142	26	9	8	5.3	5.6	9.0 ± 0.5
2-Methyl-2-propanethiol	79	138	236	6	6	18	9.8	6.4	15 ± 1.5
1-Propanethiol	14	31	49	15	18	11	3.6	9.4	3.1 ± 0.3
2-Butanethiol	19	35	55	22	13	14	4.6	14.2	3.7 ± 0.2
2-Methyl-1-propanethiol	10	17	29	29	22	17	3.7	15.8	1.9 ± 0.2

Determination of thiols dissolved in 0.01 M TBT in hexane by gas chromatography

Place a test tube of 11 cm length and 0.75 cm I.D. in boiling water and slowly add 2 ml of hexane solution. Small amounts of pulverized glass or ceramic can be added. In order to remove the hexane vapour, pass argon or nitrogen through the test tube at a flow-rate 100 ml/min for 3 min. Cool the tube and cover it with a plug containing a 0.3 cm I.D. hole. Through the hole fill the test tube with a solution prepared by saturation of 3 *M* hydrochloric acid with ammonium sulphate, until the distance to the plug is 3 cm. Close the hole with a glass rod and, keeping it tightly closed, place for 1 min in boiling water. Shake vigorously, remove the glass rod, take from the head space a 1.2-ml sample and apply it to the column.

RESULTS AND DISCUSSION

The suggested method has been extensively examined using solutions of seven thiols of concentration 10^{-5} *M* in 0.01 *M* TBT in hexane (1 ml = 10 nmol), standardized by titration with HMB. As may be seen from the results summarized in Table I, relative standard deviation varies from 4 to 29%, with an average value of about 17% for 5 nmol and 11% for 10 and 15 nmol. The proportionality between the amount of thiol taken and peak height is well confirmed within ± 10%. The relative peak area increases sharply from methanethiol to 2-methyl-2-propanethiol and then decreases. The response expressed as peak area and peak height is proportional to the amount of

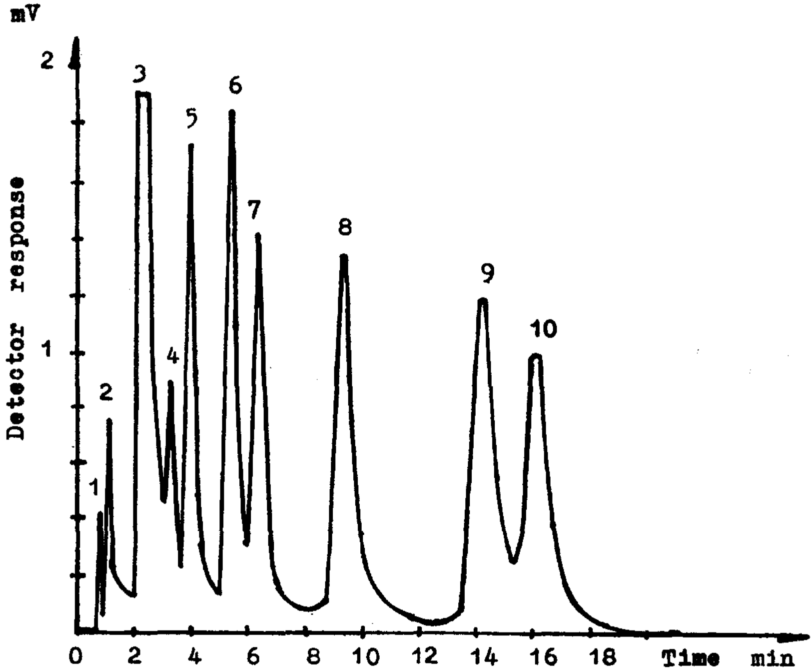

Fig. 1. Gas chromatogram of thiols separated from cigarette smoke. Peaks: 1 = methane; 2 = butane; 3 = methanethiol; 4 = hexane; 5 = ethanethiol; 6 = 2-propanethiol; 7 = 2-methyl-2-propanethiol; 8 = 1-propanethiol; 9 = 2-butanethiol; 10 = 2-methyl-1-propanethiol.

thiol taken and to its molar response for flame ionization detector. The last value increases with increasing number of carbon atoms in the molecule [11]. The volume of the headspace amounts to 1.3 ml and the volume taken for analysis 1.2 ml. When the headspace air is taken by the syringe with a simultaneous inflow of fresh air, the part of thiol taken from the head space amounts to

$$1 - \exp(-1.2/1.3) = 0.60$$

The concentration of thiol in the headspace is determined by its partition coefficient and increases with increasing temperature. The part of the total thiol content taken by the syringe as suggested in the method can be determined by absorption in alkaline alcohol solution and titration with HMB. The following results were obtained: methanethiol 12%, ethanethiol 20%, 2-propanethiol 22% and 2-butanethiol 16%.

As an illustration of the great usefulness of the suggested method, an investigation of the thiol content of the cigarette smoke was performed. A cigarette containing 0.8 g of tobacco was smoked in a stream of air, and the smoke after passing a cotton filter was absorbed, as described above, in 5 ml of 0.01 *M* TBT in hexane and 2 ml taken for analysis. The result is demonstrated on Fig. 1. It may be concluded that by this approach the thiol composition of the smoke can be clearly established. Apart from thiols traces of methane resulting from air contamination in the laboratory, butane produced by decomposition of TBT in acid solution and some remaining hexane can be seen.

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