

## Short Communication

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# Chromatographic trace analysis of some organic compounds in the environment using derivatization–sorption concentration techniques

## I. Gas chromatographic analysis of acrylates in air

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### ABSTRACT

Derivatization–sorption concentration techniques for the gas chromatographic analysis of acrylates are described. Acrylates are accumulated and derivatized in the trapping absorber. The sorption and derivatization yield of thioethers is  $71 \pm 2.6\%$ .

Two different procedures are recommended: (1) direct selective derivatization–sorption, and (2) universal sorption of all organic compounds in the first step, followed by a thermal desorption and selective derivatization in the second step.

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### INTRODUCTION

Methods for thin-layer chromatography (TLC) and gas chromatography (GC) separation of alkyl esters of acrylic and methacrylic acids [1–3] and for preparation and separation of their derivatives with diazomethane [4–6] *n*-butylmercaptan [7–9] and hydrogen chloride [10] have been published previously.

Perfect separation and identification of acrylate can be achieved by gas chromatography–mass spectrometry on an OV-101 glas capillary column [11] in less than 20 min provided, of course, a 2–10% solution of the esters is available. These conditions are impossible to meet under practical application of trace analysis. The compounds are contained in the atmosphere in concentrations of after ppm or less. In this case their direct analysis is not feasible and, consequently, it is necessary to treat the sample in order to concentrate it.

Two different procedures and their combination for identification and deter-

mination of trace amounts of acrylates in the environment have been tested in this paper.

It was demonstrated that the "trapping" procedure offers the best results if the chemical reaction and formation of derivatives are used. Universal sorption of all organic compounds on solid state sorbent (Tenax, Porapak, Separon) can help to improve the procedure further.

## EXPERIMENTAL

A number of sorbents of different origin were used as specified: Tenax GC 60–80 mesh (200–250  $\mu\text{m}$ ) was obtained from Serva (Heidelberg, Germany) Porapak S 80–100 mesh and Porapak R 80–100 mesh were purchased from Milipore Waters Chromatography Division (Milford, MA, U.S.A.), Chromosorb 102 100–120 mesh and Chromosorb 105 80–100 mesh was from Serva and Separon CHN 200–300  $\mu\text{m}$ , Separon SE 150  $\mu\text{m}$  and Separon SDA 90–125  $\mu\text{m}$  were purchased from Tessek, (Prague, Czechoslovakia). All analytical-grade solvents and pure-grade butylmercaptane were obtained from Lachema (Brno, Czechoslovakia).

### *Apparatus*

A Fractovap GW gas chromatograph (Carlo Erba, Milan, Italy) and Chrom 5 gas chromatograph–flame ionization detector (Laboratorní přístroje, Prague, Czechoslovakia) were used.

### *Enrichment procedure*

#### *Air sample collection*

*Procedure (a).* A defined amount of air (1–40 l) was sucked through the trapping absorber filled with an alkaline solution of *n*-butylthiol in acetone (sodium hydroxide concentration 0.04 mol/l, *n*-butylthiol concentration 0.03 mol/l). On-line derivatization–sorption hardware (Fig. 1a) was home-made (diffuser bubbler trapping absorber 250 mm  $\times$  25 mm O.D.).

*Procedure (b).* Glass tubes (60 mm  $\times$  3.2 mm I.D.) containing 80–140 mg of solid sorbent were used. The air was sampled at a flow-rate of 100–400 ml/min. The flow-rate was calibrated with a soap bubbler flowmeter (Fig. 1b).

*Procedure (c):* This represents a combination of procedures (b) and (a): The entrapped organic compounds (by procedure b) were desorbed by thermal desorption and flushed with inert gas into a derivatization–sorption apparatus. Of the many organic compounds which were trapped on solid sorbent, only acrylates would react in the trapping absorber. Hydrocarbons and other organic compounds (not containing a double bond) did not react and were not retained.

Absorption solution was concentrated, transferred quantitatively into 5-ml or 1-ml volumetric vessels; if the concentration of the contaminant was extremely small then it was necessary to use even smaller vials.

## RESULTS AND DISCUSSION

The role of derivatization in modern chromatographic analysis is not only to increase the sensitivity of detection but also in possibly to concentrate the substances being followed in the course of sampling.

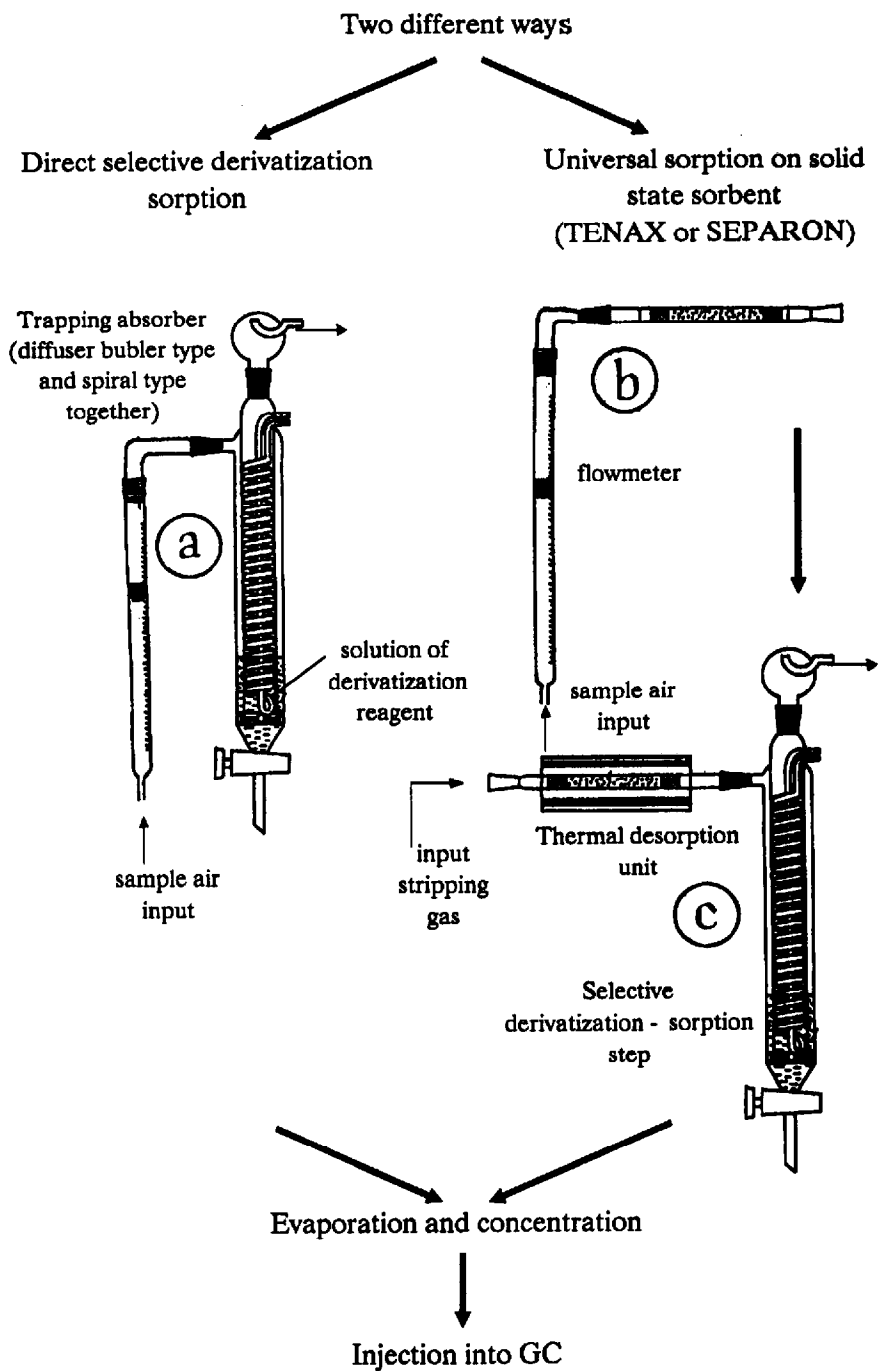


Fig. 1. A schematic representation of the sorption system assembly.

The principle of the derivatization-sorption procedure is obvious. A certain amount of air is sucked through the trapping absorber filled with the solution of the reagent (selective derivatization-sorption method) (Fig. 1a). The best are diffuser bubblers having an absorbent solution capacity of 10–100 ml working at a sampling rate from 100 ml to thousands of milliliters per minute. They are easy to use and have a good gas-liquid contact time, but are subject to plugging. One disadvantage of this method is considerable evaporation of the solvent from the absorption apparatus during suction of a larger amount of air.

This problem does not occur if the sorption tube (Fig. 1b) is used with a solid sorbent (Tenax, Porapak, Chromosorb or some new sorbent type like Separon) (Table I). In the first step, preliminary concentration is carried out. In the tube of the solid sorbent, all organic compounds contained in the air are entrapped. In the next step (Fig. 1c) the entrapped organic compounds are removed, *i.e.* desorbed, from the solid sorbent by thermal desorption and flushed with inert gas into a derivatization-sorption apparatus. Here only acrylates are selectively entrapped and concomitantly converted into corresponding derivatives. Other organic compounds pass through the reactor. The absorption solution is then concentrated, transferred quantitatively into a volumetric flask and, finally, the solution is injected into the gas chromatograph.

The main question is which reagents can be used for derivatization. In our case *n*-butylthiol and diazomethane appeared to be the best, but we limited ourselves to *n*-butylthiol.

For optimization of the sorption-derivatization process, it was necessary to take into account the following facts:

(a) The flow-rate of the air sample through the absorption unit must be kept at its optimum. In our case the optimum flow rate of the gaseous sample was 210 ml/min.

(b) The absorption (reaction) temperature must be also optimized and should represent a compromise between the need to ensure sufficiently fast reaction and tolerable evaporation of the reaction solution. Though one would propose an operating temperature of 40°C, for practical reasons we have worked at 25–35°C.

TABLE I

EXTRAPOLATED RETENTION VOLUMES ( $V_g$ ) AND SAFE SAMPLING VOLUMES ( $V_{max}$ ) [12] OF *n*-BUTYLACRYLATE ON POROUS POLYMERS

Sorbent	$V_g$ (l/g) at 293 K	$V_{max}$ (l/g) at 293 K	Ref.
Tenax GC	1630	1540	This paper
	63	32	13 <sup>a</sup>
	238	120	14 <sup>b</sup>
Porapak S	2150	1980	This paper
Porapak R	6670	6350	This paper
Chromosorb 102	1190	1120	This paper
Chromosorb 105	1490	1890	This paper
Separon SE	1140	940	This paper
Separon SDA	560	520	9
Separon CHN	4830	4210	This paper

<sup>a</sup> For methyl- and ethylacrylate.

<sup>b</sup> For methylacrylate (7.96 ml of Tenax was used).

TABLE II

RELATIVE WEIGHT RESPONSE (RWR) AND RELATIVE STANDARD DEVIATION (R.S.D.) FOR ACRYLATE DERIVATES USING FLAME IONIZATION DETECTION ( $n = 6$ )

Butylthioether of acrylic acid ester C <sub>1</sub> -C <sub>8</sub>	RWR	R.S.D. (%)
1	1.20	2.05
2	1.16	2.31
3	1.08	2.89
4	1.00	—
5	1.20	2.67
6	1.12	2.65
7	1.15	2.40
8	1.10	2.55

TABLE III

REPRODUCIBILITY OF DERIVATIZATION TRAPPING PROCEDURE BY OPTIMAL CONDITIONS

Flow: 200 ml/min; sodium hydroxide concentration: 0.04 mol/l; *n*-butylthiol concentration: 0.03 mol/l; temperature: 35°C. SA4 = *n*-butylthioether of *n*-butylacrylate;  $\rho$ SA4 = concentration (mass) of injected solution;  $c_{SA4}$  = concentration (volume) of injected solution; R.S.D. = relative standard deviation; i.u., integration unit.

SA4 sample no.	Area (A) (i.u.) A	$\rho$ SA4 (mg/ml <sup>-1</sup> )	$c_{SA4} \cdot 10^{-3}$ (mol l <sup>-1</sup> )	Yield (%)	Average yield (%)	R.S.D. (%)
1	185 307	1.628	7.457	66.07		
	185 748	1.632	7.475	66.23	66.15	0.171
2	191 863	1.686	7.721	68.41		
	190 884	1.677	7.681	68.06	68.24	0.363
3	196 424	1.726	7.904	70.04		
	195 009	1.696	7.707	68.82	69.43	1.243
4	184 572	1.622	7.427	65.81		
	189 214	1.663	7.614	67.46	66.64	1.751
5	211 200	1.856	8.499	75.30		
	218 586	1.921	8.796	77.94		
	207 178	1.820	8.337	73.87	75.70	2.727
6	215 378	1.892	8.667	76.79		
	223 153	1.961	8.980	79.57	78.18	2.514
7	190 576	1.674	7.669	67.95		
	196 650	1.728	7.913	70.12		
	201 910	1.774	8.125	71.99	70.02	2.888
8	193 489	1.700	7.786	69.00		
	197 138	1.732	7.933	70.29	69.65	1.310
9	219 130	1.925	8.818	78.13		
	194 317	1.707	7.819	69.28		
	209 066	1.837	9.413	74.54	73.98	6.016
10	211 219	1.856	8.499	75.31		
	208 470	1.832	8.389	74.33	74.82	0.926
11	199 692	1.755	8.036	71.20		
	203 366	1.767	8.183	72.51	71.86	1.289

Optimization of conditions should always be carried out for a given reagent and for each sorption apparatus. The sorption efficacy of the bubbler trapping absorber can be most simply evaluated by connecting a second absorber to the system.

### Enrichment procedure

Acrylates present in an air sample were simultaneously accumulated and derivatized in the trapping absorber. A given amount of air (1–40 l) was sucked through the trapping absorber (reactor) filled with 25–50 ml of acetone solution containing 0.04 mol/l sodium hydroxide and 0.03 mol/l *n*-butylthiol. The sorption and derivatization yield was  $71.3 \pm 2.6\%$  ( $n=10$ ). The absorption solution was concentrated and transferred quantitatively into a 5-ml volumetric flask (it is also possible to use volumetric vessels of 1 ml or less if necessary).

### Estimation of the determination limit and quantitative aspects

The limit of determination was established by using an absorption unit equipped with a stripping vessel into which 0.3–900  $\mu\text{g}$  of acrylic acid butyl ester was gradually added. The minimum amount of corresponding thioether assayed was 1.5  $\mu\text{g}$ . The relative weight response of the analysed derivatives is summarized in Table II. As indicated, the relative standard deviation for each derivative on the packed GC column

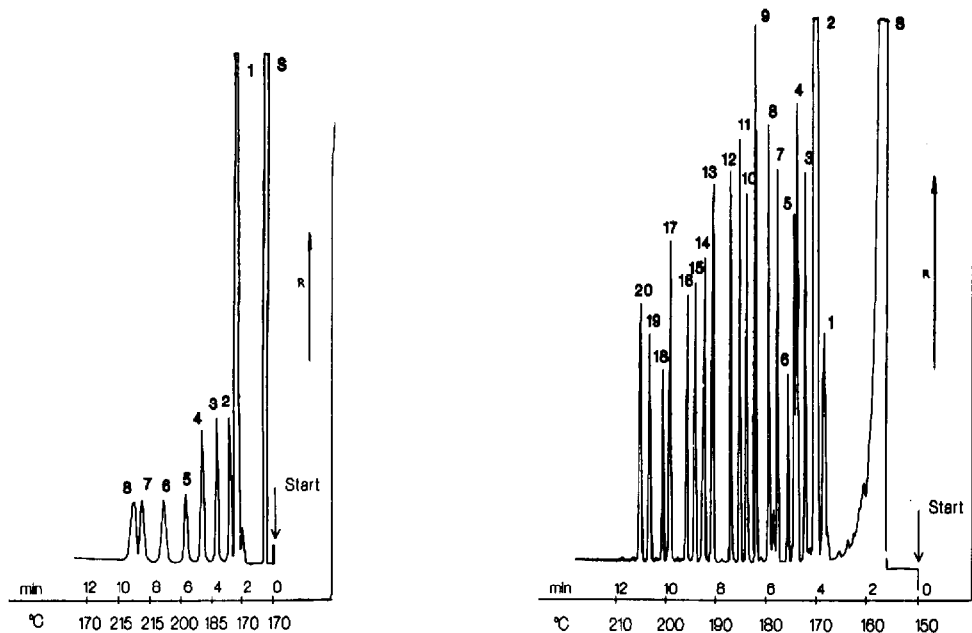


Fig. 2. GC gradient temperature separation of methyl- to octylacrylate butylthioethers (SA 1–8). Chrom 5-flame ionization detector: column 2.4 m  $\times$  3 mm I.D., Chromosorb W AW with 20% DC-200, nitrogen flow 48 ml/min, hydrogen flow 30 ml/min, air flow 500 ml/min. Temperature programme: 170°C at 2 min, 7.5°C min<sup>-1</sup>, 210°C at 2 min. S = solvent; 1–8 = methyl- to octylacrylatethioethers. R = Response.

Fig. 3. Separation of C<sub>1</sub>–C<sub>6</sub> *n*-alkyl and C<sub>3</sub>–C<sub>6</sub> isoalkyl esters of acrylic and methacrylic acid on a fused-silica capillary column. For experimental conditions and peak identification, see Table IV.

TABLE IV

RETENTION TIME ( $t_R$ ) AND RELATIVE RETENTION (RRT) OF *n*-BUTYLTHIOETHERS OF C<sub>1</sub>-C<sub>6</sub> *n*-ALKYL AND C<sub>3</sub>-C<sub>6</sub> ISOALKYL ESTERS OF ACRYLIC ACID AND METHACRYLIC ACID ON FUSED-SILICA CAPILLARY COLUMN, 32 m WITH OV-101

Temperature gradient 5°C min<sup>-1</sup>, from 150 to 220°C. Bu<sub>2</sub>S<sub>2</sub> = dibutyldisulphide; SA 1-6 = thioether from C<sub>1</sub>-C<sub>6</sub> acrylates; SMA 1-6 = thioether from C<sub>1</sub>-C<sub>6</sub> methacrylates; i = iso.

No of peak	Compound	$t_R$ (s)	RRT
S	Solvent	(88.0)	(0.16)
1	SA 1	277.5	0.52
2	SMA1 + Bu <sub>2</sub> S <sub>2</sub>	298.2	0.55
3	SA2	336.2	0.63
4	SMA2	361.6	0.67
5	SAi3	363.7	0.68
6	SMAi3	392.4	0.73
7	SA3	430.0	0.80
8	SMA3	457.0	0.85
9	SAi4	493.3	0.92
10	SMAi4	519.3	0.96
11	SA4	538.3	1.00
12	SMA4	553.2	1.03
13	SAi5	612.6	1.14
14	SMAi5	633.4	1.18
15	SA5	657.0	1.22
16	SMA5	680.7	1.26
17	SAi6	729.8	1.36
18	SMAi6	749.6	1.39
19	SA6	782.6	1.45
20	SMA6	804.3	1.49

was less than 3%. The reproducibility of the derivatization-sorption trapping procedure is shown in Table III.

#### Gas chromatographic separation

For identification and quantitative trace analysis of acrylate and methacrylate derivatives (thioethers), an analytical column packed with Chromosorb W AW with 20% DC 200 (Fig. 2) or a capillary fused-silica column with OV-101 silicone phase (Fig. 3) appeared to be the best. Retention times and relative retention times (with respect to *n*-butylacrylate) of corresponding butylthioethers are presented in Table IV. Each derivative displayed a single sharp symmetrical chromatographic peak with no significant peak tailing and did not indicate any signs of decomposition on the column.

#### CONCLUSIONS

The application of universal sorption on Tenax or Separon only does not solve the problem of determining nanogram concentrations of acrylates in 1 litre of air. This is because a great number of a whole series of organic compounds, mostly hydrocarbons, which are sorbed on a solid sorbent may be present in the sampled

atmosphere. During the desorption step these are released and flushed into the chromatographic column, resulting in much overlapping of the tiny peaks of acrylates.

Not does the application of derivatization–sorption procedures for the analysis of trace amounts of acrylates in air solve this problem because a large volume of air (100–1000 l) must be sucked through the derivatization sorption apparatus, leading to sorption solution and time losses.

To follow trace amounts of acrylates in the atmosphere, of the order of ng/l, both universal concentration techniques (sorption on solid sorbent) and subsequent selection connected with chemical derivatization should be used in combination.

Two different procedures for identification and determination of acrylates in the environment are recommended (Fig. 1):

(1) Direct selective derivatization–sorption method (Fig. 1a).

(2) Universal sorption of all organic compounds on a solid sorbent in the first step (Fig. 1b) followed by a thermal desorption and selective derivatization sorption in the second step (Fig. 1c).

The main advantage of the second procedure is that, of the many organic compounds which are trapped on the solid sorbent, only acrylates will react with *n*-butylthiol.

The last step is common to both procedures: the sorption solution is partly evaporated, the entrapped solutes are concentrated and the resulting sample is subjected to GC analysis.

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