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Note

Photometric monitoring of thiols by means of a thiomercurimetric detector

MIECZYŚLAW WRÓŃSKI* and LONGIN WALENDZIAK

Department of Chemical Technology, University of Łódź, Nowotki 18, Łódź (Poland)

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The selective monitoring of thiols after their chromatographic separation is of importance in the analysis of complex mixtures, and procedures based on the change in potential of a platinum electrode in the presence of the iodide-iodine system¹ or the change in potential of a mercury electrode² have been suggested. The relationship between change in potential and thiol concentration is not linear and depends on pH. Thiols in natural gas have also been monitored by automatic titration with coulometrically generated silver ion³.

The method proposed in this paper is based on the displacement of dithiofluorescein from its complex with *o*-hydroxymercuribenzoic acid (HMB)⁴. In alkaline solution dithiofluorescein has a blue colour, which disappears on adding HMB and reappears on adding thiols or hydrogen sulphide.

EXPERIMENTAL AND RESULTS

Materials

Solution of the HMB-dithiofluorescein complex. Dissolve 0.16 g of *o*-hydroxymercuribenzoic acid anhydride (POCh, Poland) in 100 ml of 5% (w/v) diethanolamine solution. Dissolve separately 0.1 g of dithiofluorescein (POCh) in 100 ml of 5% (w/v) diethanolamine solution. Take 20 ml of the first solution and add slowly with mixing the second solution until a distinct blue colour persists, filter rapidly, add 500 ml of 96% ethanol and dilute to 1 l with 5% (w/v) diethanolamine solution. The solution should have a slight blue colour, otherwise add a portion of filtered dithiofluorescein solution. The complex solution is $2 \cdot 10^{-4}$ M with respect to HMB and gives a linear absorbance response on adding thiols or hydrogen sulphide until *ca.* 90% of the dithiofluorescein is displaced. The solution should be protected from light.

Thiol solutions. Solutions of thiols were prepared in *n*-hexane and standardized by titration with HMB in the presence of dithiofluorescein as indicator⁴.

Thiomercurimetric detector in gas chromatography

Details of the combination are illustrated in Fig. 1. The thiols emerging from the column in a stream of carrier gas are absorbed in vessel 3 in a solution of the complex which is forced from vessel 1. The solution containing absorbed thiol passes

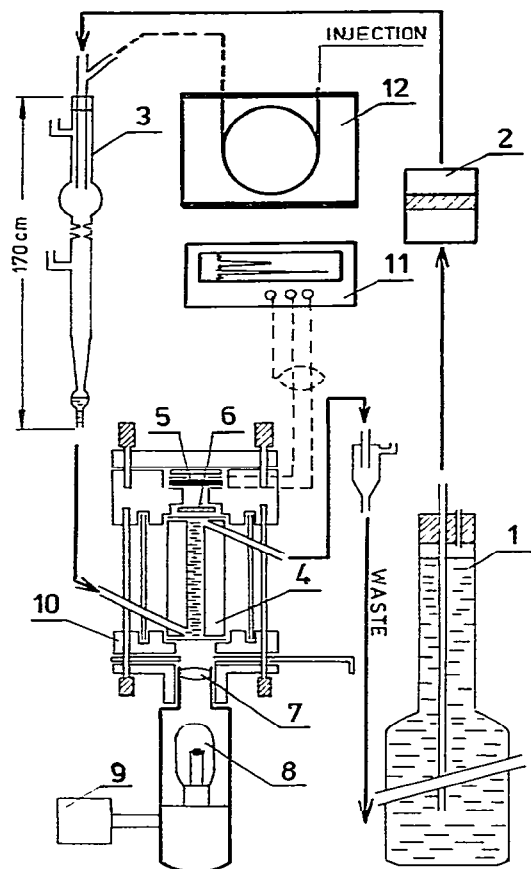


Fig. 1. Thiomercurimetric detector combined with a gas chromatograph. 1, Container for complex solution; 2, pump; 3, absorption column; 4, flow-through cell, 50-mm light path, 3 mm I.D.; 5, photocell; 6, optical filter (580 nm); 7, collimator; 8, light source, 6 V/15 W bulb; 9, transformer; 10, cell holder made of hard resin; 11, TZ-216 recorder (Czechoslovakia); 12, Chrom 41 chromatograph (Czechoslovakia).

to the lower part of vessel 3 and then to the flow cell, while the gas is removed by the two side-tubes. The current of the photocell is compensated by an anti-current and the recorder is then at zero. When the absorption of light in the flowing solution increases the current of the photocell will be decreased and the deflection of the recorder corresponds to the difference between the photocell current and anti-current. Let H be the full deflection of the recorder from the zero line and h the actual deflection. Then the absorbance will be expressed by $\log [H/(H - h)]$, and the concentration of thiol by $\log [H/(H - h)] \cdot \text{constant}$. The total amount of the thiol can be calculated from the equation

$$m = K\Delta V \cdot \log [H/(H - h_m)]$$

where m = total amount of thiol (moles), K = a constant for a given detector valid for all thiols, h_m = peak height and ΔV = basis of the peak (ml).

The value of the K has to be found by standardization which is demonstrated in Table I and Fig. 2. Known amounts of n -propanethiol were injected on to the column of the gas chromatograph and the resulting peaks were recorded by the thiomercurimetric detector. The mean value of K thus found was 14 nmole/ml.

TABLE I

STANDARDIZATION OF THE THIOMERCURIMETRIC DETECTOR WITH n -PROPANETHIOL ACCORDING TO RESULTS IN FIG. 2

Full-scale deflection of recorder = 200 mm.

Injected (nmole)	ΔV (ml)	h_m (mm)	K (nmole/ml)
5.2	15.7	11	13.7
10.4	12.6	25	14.2
20.8	10.5	55	14.2
31.2	10.5	78	13.9
41.6	10.4	97	14.1
52.0	10.5	112	13.8

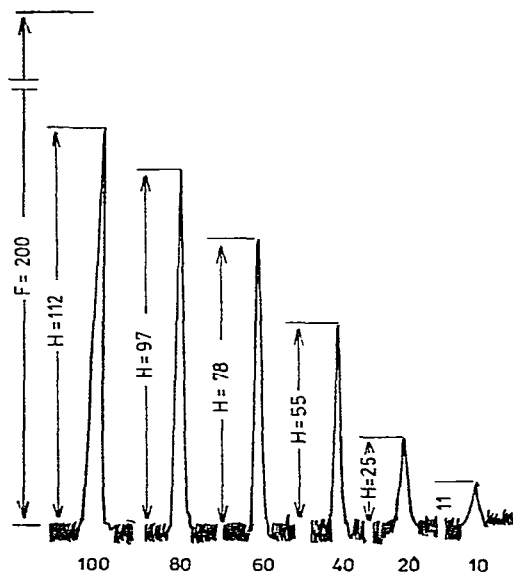


Fig. 2. Standardization of the detector by injection of 10, 20, 40, 60, 80 and 100 μ l of $5.2 \cdot 10^{-4}$ M n -propanethiol in n -hexane. Details as in Fig. 3.

Fig. 3 shows a typical chromatogram for a thiol mixture obtained with the thiomercurimetric detector, and Table II gives the corresponding amounts of thiols calculated for $K = 14$ nmole/ml. The deviations ranged from -2 to -11% . For more accurate analysis internal standardization is necessary.

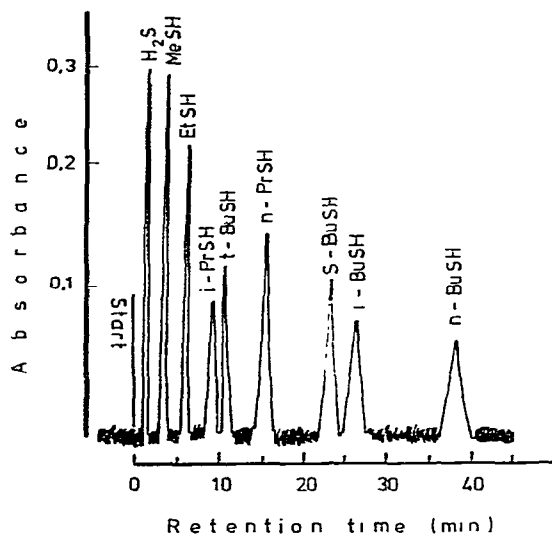


Fig. 3. Gas-liquid chromatogram of standard mixture of thiols in *n*-hexane. Column, 2.5 m \times 3 mm I.D., glass, packed with 25% tricresyl phosphate on 80-120-mesh Celite. Temperature, 327°K; injector temperature, 353°K; detector, thiomercurimetric; complex solution flow-rate, 4.2 ml/min; carrier gas, nitrogen at 17 ml/min.

TABLE II
CALCULATION OF THIOL CONTENTS FROM FIG. 3

Thiol	ΔV (ml)	h_m (mm)	Injected (nmole)	Found (nmole)
Methanethiol	4.2	96	16.8	16.5
Ethanethiol	4.6	77	14.7	13.5
Isopropanethiol	8.6	35	10.2	9.8
<i>tert.</i> -Butanethiol	9.2	45	14.7	14.1
<i>n</i> -Propanethiol	9.5	53	18.2	17.6
<i>sec.</i> -Butanethiol	11.5	42	18.2	16.3
Isobutanethiol	12.6	30	13.7	12.2
<i>n</i> -Butanethiol	16.5	26	15.1	13.8

Monitoring of thiols in high-performance liquid chromatography

The liquid eluate leaving the chromatograph is mixed with the complex solution and the mixture is passed to the detector. The chromatograms obtained are shown in Figs. 4 and 5. It can be concluded that the detector is suitable for recording thiols separated by liquid chromatography.

DISCUSSION

The detector can also be used for silylated thiols because in the complex solution the sulphhydryl group is quickly regenerated. In the presence of dimethylamine thiol esters are also recorded. Other compounds to which the detector can be applied

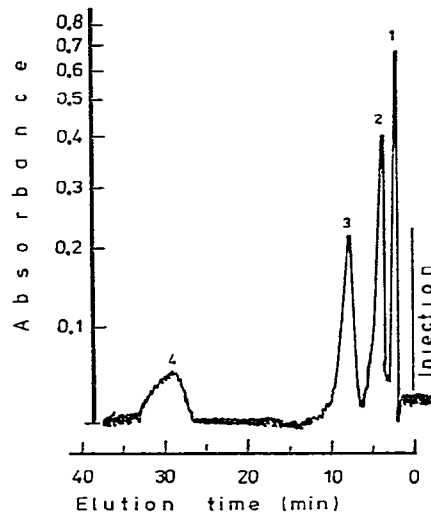
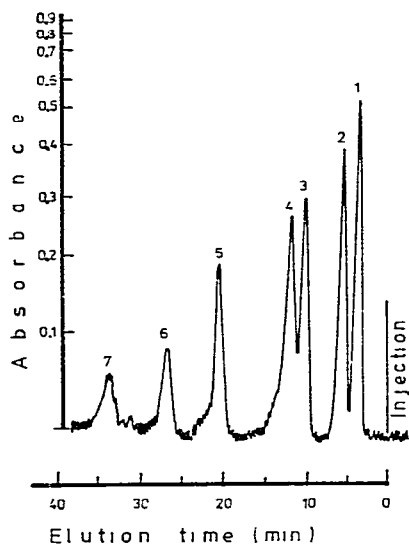


Fig. 4. Chromatogram of thiols obtained with an ALC-204 high-performance liquid chromatograph (Waters Assoc., Milford, MA, U.S.A.). Column, 30 cm \times 3.9 mm I.D., packed with μ Bondapak C_{18} . Temperature, 295°K; detector, thiomercurimetric; complex solution flow-rate, 1.4 ml/min; eluent, 75% methanol, flow-rate 4 ml/min. Peaks: 1 = CH_3SH ; 2 = C_2H_5SH ; 3 = *iso*- C_3H_7SH ; 4 = *tert.*- C_4H_9SH ; 5 = *n*- C_3H_7SH ; 6 = *sec.*- C_4H_9SH ; 7 = *n*- C_4H_9SH .

Fig. 5. As Fig. 4. Peaks: 1 = *n*- $C_5H_{11}SH$; 2 = *n*- $C_6H_{13}SH$; 3 = *n*- $C_9H_{19}SH$; 4 = *n*- $C_{12}H_{25}SH$.

are dithiocarbamates, carbon disulphide, carbonyl sulphide and compounds that can be readily converted to thiols or hydrogen sulphide.

The sensitivity of the detector is about 2 nanomole of thiol.

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