GAS CHROMATOGRAPHIC ANALYSIS OF MERCAPTANS USING THE ION-SELECTIVE ELECTRODE DETECTOR

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An electrochemical ion-selective electrode detector in conjunction with the gas chromatograph and the TCD in series is described and its operating characteristics are discussed. Under optimal conditions for resolution, mercaptans are absorbed in $1 . 10^{-4}$ mol l^{-1} $AgNO_3$ absorption solution at a flow rate 1·2 ml min^{-1} and detected by Ag_2S- solid membrane electrode. The detection limit $6 . 10^{-11}$ mol S calculated for propyl mercaptan is achieved, however, only in $1 . 10^{-5}$ mol l^{-1} $AgNO_3$, where a poor resolution of mercaptane occurs. Other parameters affecting the separation and sensitivity are flow rate of absorption solution and geometry of the cell and of the absorber.

The selective and highly sensitive detection of sulfur containing compounds is often required, especially in the high concentrated hydrocarbon matrices. A number of element-selective detectors is well known: The flame photometric detector (FPD) for sulfur and phosphorus is probably most popular, however its possibilities are limited if the heavier hydrocarbons are present in the sample[1,2]. The Hall electrolytic conductivity detector (HECD) is recommended instead of the FPD (ref.[3]). The linear range of this detector is at least of one order higher and sensitivity more than 20 times higher than those of FPD (ref.[3,4]). Recently, electrochemical flow-through detectors have become popular in liquid chromatography and flow-injection analysis[5]. The incorporation of ion-selective electrodes (ISE) into continuous systems provides the effective means for direct determination of ions and molecules. Several general papers have appeared which refer to various aspects of such systems[6-8]. ISEs were successively used as detectors in the ion-exchange liquid chromatography[9-11], ion-chromatography[12] and in open tubular column liquid chromatography[13].

Application of ISESs in gas chromatography was first described by Kojima and coworkers[14-20]. Compounds containing chlorine, bromine, fluorine, sulfur, and nitrogen can be detected using the appropriate ISE. The principle is allways the same: the sample is post-column hydrogenated in a Pt-capillary tube at $800-1\,000°C$

with hydrogen stream, and hydrogen halogenides, H_2S or NH_3 formed are absorbed in a suitable absorption solution. The excess gas is separated, and the solution is led into the detector cell. The detector is sensitive to 10^{-12} mol of sulfur, 10^{-10} mol of chlorine, and 10^{-11} mol of fluorine compounds[20]. The Ag_2S-ISE in connection with the gas chromatograph was also used for continuous H_2S monitoring of the coke oven gas[21].

Mercaptans can be directly detected using $AgNO_3$ absorption solution and Ag_2S--ISE. The GC separation of mercaptans is well achieved in a stainless steel column packed with acetone washed Porapak QS as suggested in the literature[22]. The time response of the ISE is slowed down with decreasing concentration of the electrolyte and its flow rate.

In the present paper, the construction of a versatile flow-through detector, with only 10 µl dead volume, and the optimization of chromatographic separation are discussed.

EXPERIMENTAL

Gas chromatograph MCH-112 with TCD (Chemoprojekt, Prague) operated at 220°C and hydrogen as the carrier gas with a flow rate 30 ml min^{-1} were used. The stainless steel column 2 m $\times$ $\times$ 3 mm was packed with acetone washed Porapak QS 120—150 mesh (Waters, USA). A sample was applied by 0·5 or 1 µl Hamilton syringes. The absorption solution was pumped by a single piston high pressure pump VCM 300 (ČSAV, Prague) to the absorption tube (a glass capillary 15 cm $\times$ 1 mm) with a gas–liquid separator (1·3 cm wide and 2·5 cm long), similar to that used previously[20]. ISE detector was equipped with Ag_2S-ISE Crytur (Monokrystaly, Turnov, ČSSR), and a precission digital pH/mV-meter OP 208 (Radelkis, Hungary) was used in conjunction with the recorder TZ 4100 (Laboratorní přístroje, Prague). Mercaptans (Ega-Chemie, FRG) and all other chemicals were of analytical grade. Silver nitrate solutions of various concentrations were obtained by dissolving the salt in a buffer containing 0·25 mol l^{-1} NH_3 and 0·1 mol l^{-1} NH_4NO_3 in methanol.

RESULTS AND DISCUSSION

The general scheme of the apparatus is shown in Fig. 1. The effluent is led to the absorption tube, where it causes the segmentation of the liquid solution flow. After being separated from the gas, the liquid flows down to the cell. Thus, absorption tube presents a special type of air-segmented reactor, where the reaction does not occur in the liquid phase, but on the phase boundary between the liquid and the gas.

The construction of the flow-through cell is schematically drawn in Fig. 2. The hole cut in the polyethylene plate forms the cell volume (in all measurements the fixed volume of 10 µl was used). The thread on a commercial electrode was made with the aid of epoxide resin.

The potentiometric determination of mercaptans is a serious problem in general, due to their non-stoichiometric reaction with Ag^+ ions, with a strong adsorption

of Ag^+ ions on precipitates (mercaptides) as well as on the apparatus material[23,24]. The higher mercaptans are practically insoluble in water and they are stable only in strong basic solution, and therefore the ammonia-methanolic solution has been chosen. In this solution $AgNO_3$ can be easily dissolved forming $[Ag(NH_3)_2]^+$ complex cation.

Fig. 3a shows the response of ISE detector to mercaptans as a function of the absorption solution flow rate. At a small flow rate, mercaptans separated in the GC column are absorbed in a rather small volume of the liquid. In this case, the sensitivity is very high, however, the dispersion in the separator and in the detector plays an important role, and the resulting chromatogram shows overlapped peaks. The separation is improved with increasing flow rate, but sensitivity is decreased. Another important factor affecting the detector efficiency is the concentration of $AgNO_3$ (Fig. 3b). At $1 . 10^{-3}$ mol l^{-1} $AgNO_3$ the loss of Ag^+ ions is low, according to the total amount present in the buffer, and that is why the low detector response is observed. On the other hand, dispersion effects are negligible, and the resolution of com-
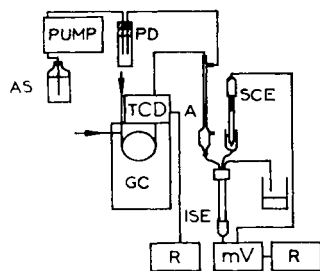

Fig. 1

Schematic diagram of the apparatus. (GC) gas chromatograph, (TCD) thermal conductivity detector, (AS) absorption solution, (PUMP) single piston reciprocating pump, (PD) pulse damper, (A) absorption tube with gas-liquid separator. (ISE) electrode body with the cell, (s.c.e.) saturated calomel electrode with saturated KNO_3 salt bridge. (mV) pH/mV-meter, (R) recorder
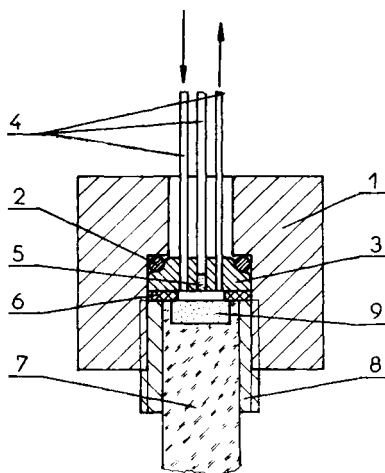
Fig. 2

Construction of the flow-through cell with the ISE. (1) detector body made of plexi-glass, (2) silicone O-ring, (3) epoxide holder of capillaries, (4) inlet, outlet capillaries with capillary for s.c.e., (5) small frit cemented into the capillary, (6) polyethylene plate, (7) ISE body, (8) epoxide thread, (9) Ag_2S-solid membrane

pounds is unchanged. The TCD as a universal detector possesses lower sensitivity than any other sulfur selective detector (*e.g.* HECD, FPD, photoionization detector), and since it is a non-destructive detector it can be connected in series with the ISE detector. This arrangement is required for the direct monitoring of the flow-dispersion phenomenon and the selectivity of the system. The response of an ISE is the logarithmic function of the concentration of measured ions. Therefore, elution profiles often look much broader and show more overlap than elution profiles obtained with conventional linear responsive detectors[13].

In Fig. 4 the chromatograms of mercaptans obtained with both TCD and ISE detectors are shown. The resolution value $R_{1,2}^{TCD}$ at least of 1·3 is needed for GC separation to achieve the appropriate resolution value $R_{1,2}^{ISE}$ of 0·9 for ISE detector. This is illustrated for propyl mercaptan and isopropyl mercaptan (peaks 2, 3). The selectivity of ISE detector is evident: the high solvent peak (methanol and water) detected by the TCD is diminished when detected by ISE detector.

Fig. 5 shows the calibration curves for propyl mercaptan. If $1 . 10^{-4}$ mol l^{-1} $AgNO_3$ is used, the quasi titration curve for SH^- and Ag^+ ions is obtained (curve 2).
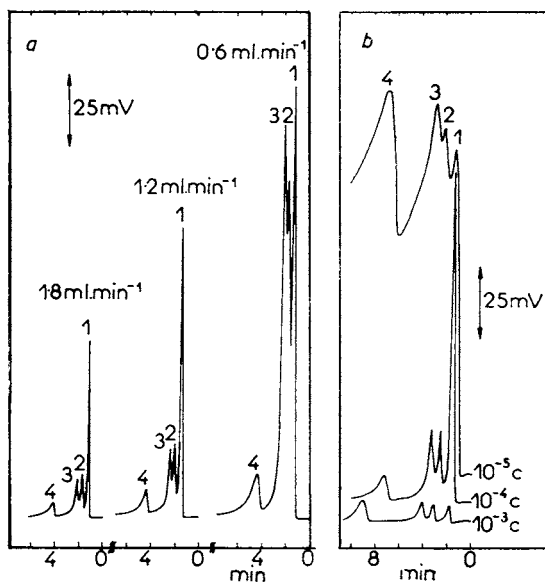

FIG. 3

Response of ISE detector as a function of (*a*) the flow rate and (*b*) concentration of the absorption solution. Experimental conditions: (*a*) 1 m column packed with Porapak QS, $1 . 10^{-4}$ mol . l^{-1} $AgNO_3$ solution, (*b*) 2 m column packed with Porapak QS, constant flow rate 0·6 ml . min^{-1}. Peaks: (1) ethyl mercaptan, 108 nmol, (2) propyl mercaptan, 43 nmol, (3) isopropyl mercaptan, 66 nmol, (4) 2-mercaptoethanol, 456 nmol, volume injected 0·2 μl

The reaction equilibrium in a segmented volume of the liquid is reached in the inflection point, and Ag_2S-ISE becomes sensitive to the excess of SH^- anions at higher concentrations of propyl mercaptan. It is not possible to linearize this sigmoidal calibration curve since the Nernst equation is not valid near to, and in the reaction equilibrium. This serious drawback can be overcome *e.g.* using the absorption solution of higher concentration (curve *1*). In this case the sensitivity of the detector is decreased more than 10 times as compared with curve *2*, but the curve *1* is in a good agreement with the Nernst equation. For lower concentrations of $AgNO_3$ than $1 . 10^{-4}$ mol$\,$l^{-1} the ISE is not capable of being quickly regenerated which causes the tailing of peaks (shown in Fig. 3b), and thus practically no resolution is achieved. However, if only one mercaptan is to be analyzed, it is convenient to use $1 . 10^{-5}$ mol$\,$l^{-1} $AgNO_3$ absorption solution with detection limit $6 . 10^{-11}$ mol S (calculated from signal 2 times higher than noise) for propyl mercaptan. If $1 . 10^{-4}$ mol$\,$l^{-1} $AgNO_3$ is used, the detection limit is $4 . 10^{-9}$ mol S for the same compound.
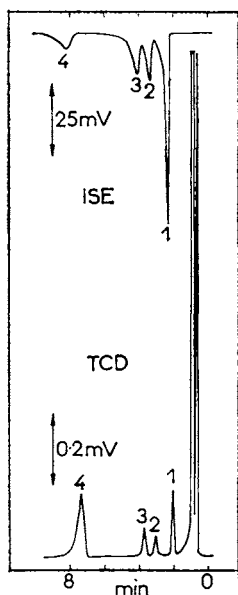

Fig. 4

Simultaneous chromatograms of TCD and ISE detector. Experimental conditions: for TCD and GC as in Experimental, 2 m column packed with Porapak QS, $1 . 10^{-4}$ mol$\,$l^{-1} $AgNO_3$ solution at a flow rate 1·2 ml min^{-1}. Peaks: as in Fig. 3
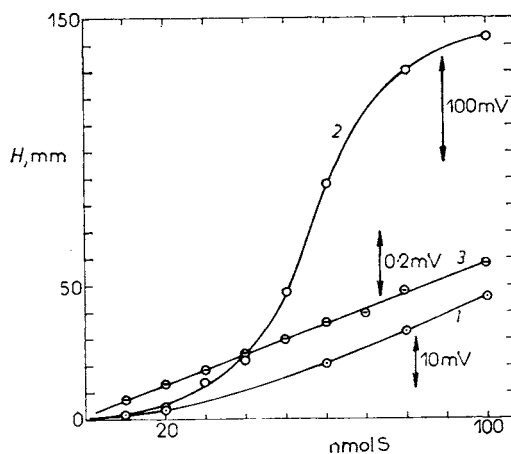

Fig. 5

Calibration curves of propyl mercaptan detected *1*, *2* by ISE detector, or *3* by TCD. Experimental conditions: for TCD and GC as in Experimental, 1 m column packed with Porapak QS, $c(AgNO_3)$ in absorption solutions (mol$\,$l^{-1}): *1* $1 . 10^{-3}$, *2* $1 . 10^{-4}$. H peak height (mm)

Reproducibility calculated from 5 injections was better than 5% in all cases. The detection limits reported in the literature for the FPD $(ref.^{25})$ are $8.7 \cdot 10^{-13}$ mol S, for the HECD $(ref.^{26})$ $1.6 \cdot 10^{-12}$ mol S and for the ECD $(ref.^{27})$ $3 \cdot 10^{-11}$ mol S. In this study the detection limit calculated as sulfur content of the particular compound is slighly higher than reported in the literature[20]. However, such detection limit is only achievable on account of mercaptans resolution. In this case, the detector is usable, *e.g.* for analysis of the odorized natural gas. On the other hand, if complex mixture of mercaptans should be analyzed, the higher flow rate and higher concentration of $AgNO_3$ and/or long packed or capillary column should be used. Furthermore, the linearization of the signal is possible if the antilog converter is employed. The main advantage of the ISE detector is its selectivity which is the highest one among current element selective chromatographic detectors.

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