CHROM. 10,113

Note

Significance of the rubidium bromide thermionic detector equipped with a gate electrode in the analysis of halogenated dithiocarbamate derivatives

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(First received June 18th, 1976; revised manuscript received March 29th, 1977)

During the last 10 years, the development of new and more reliable thermionic detectors has increased rapidly, and this topic has been reviewed by Krecjči and Dressler[1], Brazhnikov *et al.*[2] and Maier-Bode and Riedmann[3].

The aim of this work was to establish a gas chromatographic (GC) detection method which could improve the identification of halogenated and non-halogenated dithiocarbamate benzyl esters. In tracing sodium dimethyldithiocarbamates and sodium diethyldithiocarbamates as metabolites of tetramethylthiuram disulphide (TMTD) and tetraethylthiuram disulphide (TETD), respectively, in serum and urine, derivatization into the corresponding dichlorobenzyl and pentafluorobenzyl esters yielded compounds which showed a different behaviour in a nitrogen flame-ionization detector (NFID) equipped with a gate electrode. The basis of this work was conceived earlier by Svojanovský and co-workers[4–6]. Using a home-made thermionic detector, they found an inversion of the thermionic system signal on changing the polarities around the jet and the collector. In studying the peak inversion phenomenon with dithiocarbamate esters, we found that all gas chromatographic peaks did not show inversion at the same gate electrode potential.

EXPERIMENTAL

Reagents

For the synthesis of the dithiocarbamate esters we used sodium dimethyldithiocarbamate dihydrate (Aagrunol, Groningen, The Netherlands), sodium diethyldithiocarbamate trihydrate (Merck, Darmstadt, G.F.R.), benzyl chloride (UCB, Brussels, Belgium), dichlorobenzylbromide (Fluka, Buchs, Switzerland) and pentafluorobenzyl bromide (Pierce, Rockford, Ill., U.S.A.).

Synthesis

To a solution of 1.00 g of sodium dialkyldithiocarbamate in 96% ethanol, 250 mg of halogenide were added. This solution was kept at room temperature overnight. The dithiocarbamate ester was extracted with dichloromethane after adding an equal amount of water to the alcoholic solution. The dichloromethane phase was washed twice with doubly distilled water and dried over sodium sulphate. After evaporation to dryness, the residue was investigated for identity and physiochemical properties by means of gas chromatographic, mass spectrometric, nuclear magnetic resonance, ultraviolet and infrared measurements. The structures of and abbreviations used for the compounds synthesized are shown in Fig. 1.
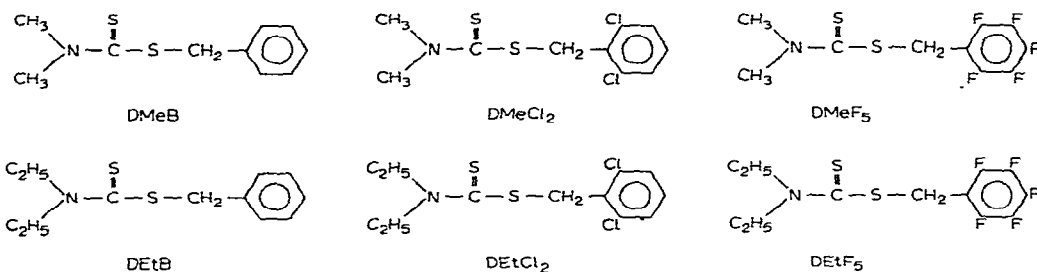
DMeB   DMeCl$_2$ DMeF$_5$

DEtB   DEtCl$_2$ DEtF$_5$

Fig. 1. Structures and abbreviations of the six compounds used.

Standard solutions

A standard series of each ester in methanol was prepared in the concentration range between 5 and 2000 ng/μl. The DMeCl$_2$, DEtCl$_2$, DMeB and DEtB solutions were spiked with 20 ng/μl of azobenzene and 5000 ng/μl of octadecane, which served simultaneously as internal standard and as an indicator for variations in the NFID conditions.

The DMeF$_5$ and DEtF$_5$ solutions, however, were spiked only with azobenzene (20 ng/μl), because of interference with octadecane. Daily, before operating the NFID, a test solution of 10 ng/μl of azobenzene and 5000 ng/μl of octadecane in n-hexane was used to monitor and to optimize the detector performance.

Materials

A Hewlett-Packard Type 5750 G research chromatograph equipped with a rubidium bromide Type 15161B NFID and a variable gate electrode potential was used (Figs. 2 and 3). The potential of the gate electrode can be varied manually and the digit numbers are calibrated by means of a voltmeter; gate potential readings are therefore expressed in volts. In order to quarantee long-term stability of the hydrogen flow we preferred a Type DRLS 7 reduction valve with a Type 0.2/20-RYA 2G precision valve (Air Liquide, Paris, France). Chromatograms were recorded with an HP 7128 recorder.

GC conditions

A Pyrex glass column (6 ft.) packed with 5% DC 200 on HP Chromosorb AW HMDS, was used. The carrier gas was helium at a flow-rate of 20–30 ml/min, with a hydrogen flow-rate of 17 $\pm$ 0.05 ml/min and an air flow-rate of 180 $\pm$ 0.2 ml/min. The
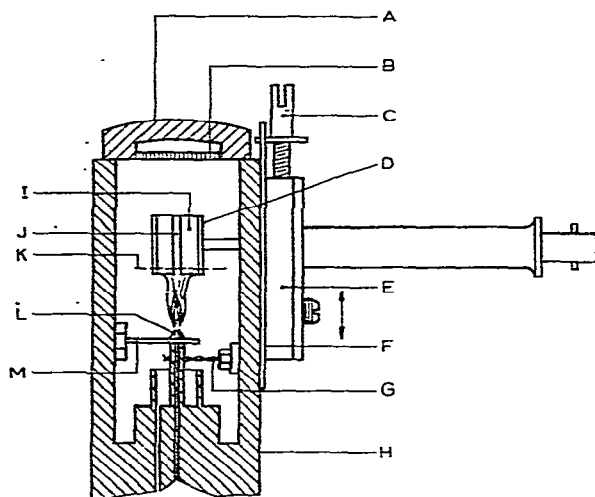
Fig. 2. RbBr NFID with gate electrode. A = Chimney cover; B = asbestos disk; C = adjustment nut; D = platina collector electrode (negative); E = collector assembly; F = guide plate; G = jet connectors; H = detector block; I = RbBr; J = central hole; K = crystal split direction; L = burner jet (positive); M = gate electrode (negative).
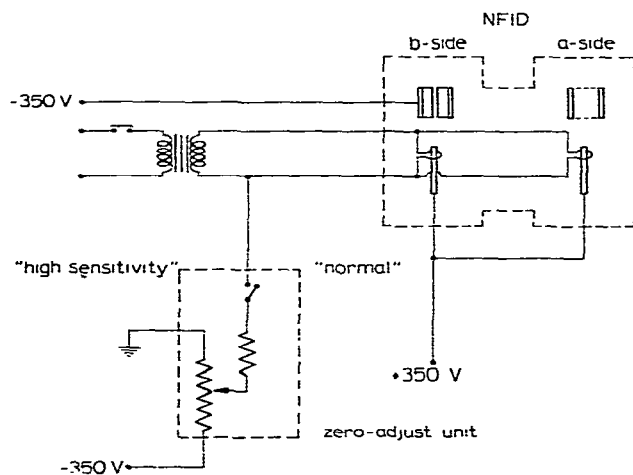

Fig. 3. Connections to gate electrode.

by-pass gas (helium) flow-rate was 40 ± 0.5 ml/min. The injection port was maintained at 260°, the column at 230° and the detector at 450°. The potentiometer setting was 48–52 and the attenuation setting $32–8 \cdot 10^2$. The zero adjust (gate electrode) was set in the high-sensitivity mode.

Influence of the gate electrode potential on NFID response and peak performance

By peak inversion we mean a gradual deformation of a chromatographic peak as a function of the applied voltage on the gate electrode (Figs. 4 and 5). The inversion zone is defined by the gate electrode potential range between the onset and the end of
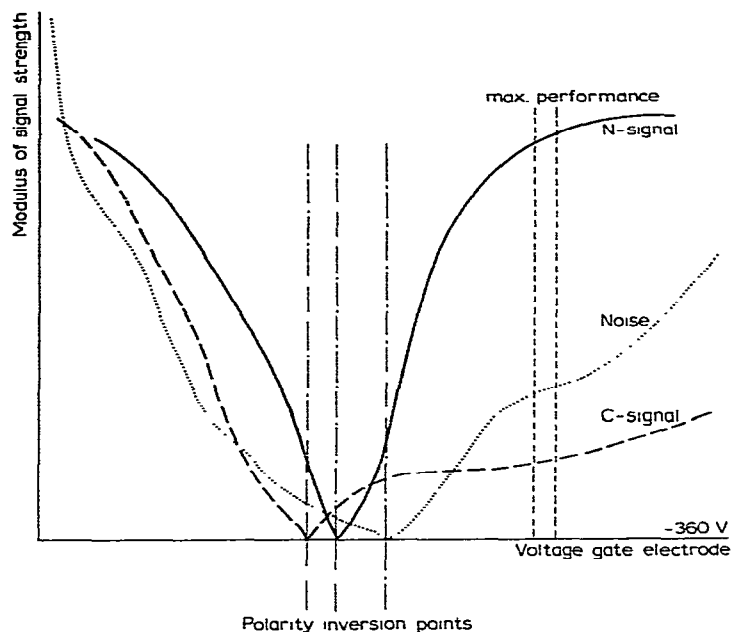
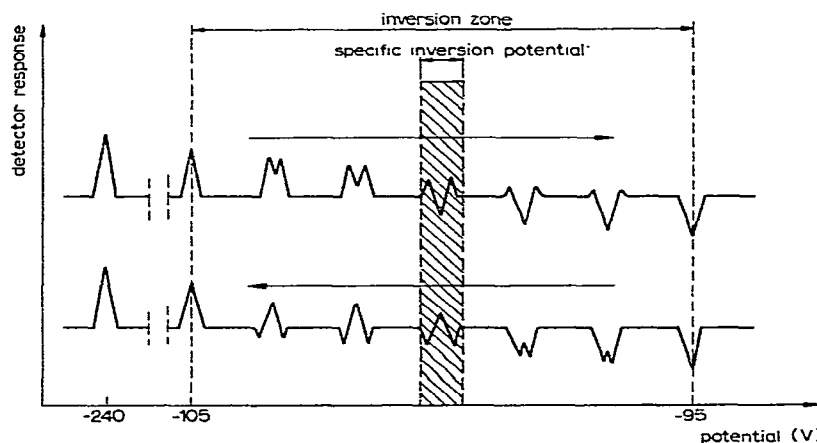Fig. 4. Change in peak response as a function of gate electrode potential.

Fig. 5. Peak shape deformation and inversion as a function of gate electrode potential.

peak inversion. The arithmetic mean of this inversion zone is called the specific inversion potential and is characteristic for each test compound investigated.

Solutions of each type of ester, containing a mixture of the dimethyl- and diethyldithiocarbamate derivatives, were injected after every change in gate electrode potential. Starting from —350 V the potential was increased by 20-V steps. When a significant reduction in peak size was observed, the potential was subsequently changed in smaller steps. The peak inversion was clearly visible and, what is of major importance, the inversion of the peak of each separate test compound was observed at different potentiometer settings. In order to establish the influence of the detector parameters on

changes in a compound's specific inversion potential, a mixture of azobenzene and octadecane was added to every test solution (see *Reagents*). The ratio of the area of the azobenzene peak to the area of the octadecane peak acted as an indicator of unexpected variations in the detector parameters. Before each new injection, the gate electrode potential was adjusted to -240 V and was kept at this potential during the elution of azobenzene and octadecane but immediately afterwards the potentiometer was re-adjusted to the desired potential (Fig. 6).
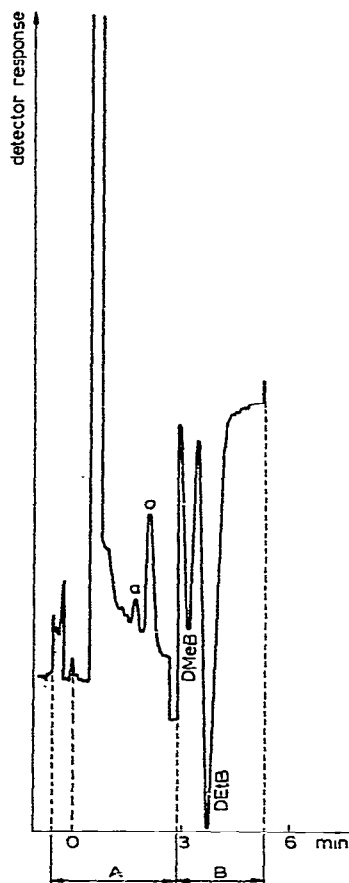

Fig. 6. Features of gas chromatogram during determination of the inversion zone. A, Gate potentia -240 V; B, gate potential at desired value. a, azobenzene; o, octadecane.

About 200 injections were made under the above-mentioned conditions and clearly demonstrated that the detector parameters, in relation to release of Rb^+, do not influence the specific inversion potential. Attempts to give each test compound a fixed specific inversion potential were unsuccessful, which can be attributed to an inadequate accuracy of the voltage supply to the gate electrode. Insertion of a digital voltmeter in the voltage supply circuit should overcome this important shortcoming. The only means of obtaining an accurate idea of the different behaviours of the six dithiocarbamate derivatives on changing the gate electrode voltage is to effect simultaneous

injection of all of the compounds. On doing so, we were able to determine the exact sequence of inversion while gradually changing the potential in the expected inversion zone after each injection. Only by observing the peak shapes an inversion sequence series was established under controlled detector conditions (Fig. 7).
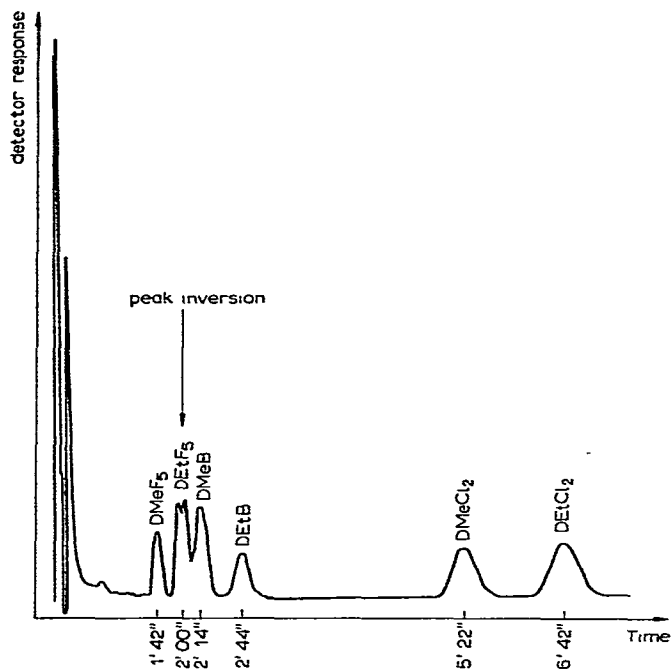

Fig. 7. Gas chromatogram showing that peak inversion takes place at a different gate electrode potential. This example was recorded at the maximum crystal position. Under these conditions and while changing the gate potential from -130 to $-70V$, DEtF$_5$ inverts first.

Although we found no major influence of the detector parameters on the stability of the inversion potential, there was some relationship between the crystal height and the inversion sequence. From the results obtained from about 100 injections of four compound mixtures we observed considerable changes in the inversion sequence when the rubidium bromide crystal was slowly turned downwards into the flame (Table I).

TABLE I

CHANGES IN INVERSION SEQUENCE ON CHANGING CRYSTAL HEIGHT

Crystal position: degrees turned anticlockwise*	Inversion sequence, screening from -130 to -70 V of 4 test compounds
Max. crystal position	DEtF$_5$, DEtB, DMeCl$_2$, DEtCl$_2$
Crystal position screw drive 270°	DEtB, DEtF$_5$, DEtCl$_2$, DMeCl$_2$
Crystal position screw drive 450°	DEtCl$_2$, DEtB, DMeCl$_2$, DEtF$_5$
Crystal position screw drive 630°	DEtCl$_2$, DMeCl$_2$, DEtB, DEtF$_5$

* From top to bottom in this column represents a decreasing distance between the crystal surface and the burner tip.

From further examination of the gas chromatograms, we noticed that the dimethyldithiocarbamate esters are inverted before the diethyldithiocarbamate esters at high crystal positions (low ratio of area of azobenzene peak to area of octadecane peak).

CONCLUSION

Each compound, depending on its heteroatom content, inverts at a different gate electrode potential, which might be best observed by injecting a series of analogous compounds, acting as internal standards, and with a controlled release of Rb^+ at the crystal surface. Very accurate control of the voltage supply to the gate electrode around the flame tip would provide the possibility of collecting fixed inversion potentials, characteristic for compounds with a certain heteroatom constitution. In searching for a more specific identification of derivatized dithiocarbamates by selective GC techniques, we think that the peak inversion phenomenon may make a valuable contribution to this kind of selective analysis methodology.

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