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Electrolytic conductivity detector for selective detection of chlorine-containing compounds in liquid chromatography

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Abstract

The use of an electrolytic conductivity detector for chlorine-specific HPLC detection is described. The use of a miniaturized LC system with flow-rates up to 60 μl/min allows the entire column effluent to be fed into the detector. The design of the laboratory-made interface supporting the vaporization process by nebulizing the eluent is described in detail. Various parameters were evaluated to determine the performance of the coupling, also applied to environmental analysis. The detector is shown to be sensitive to 52–123 pg of chlorine in chlorine-containing compounds eluted by normal-phase HPLC.

1. Introduction

High-performance liquid chromatography (HPLC) is often limited by the lack of appropriate detectors specific to a class of compounds. Especially in environmental analysis, selective detection is desirable for minimizing extensive sample clean-up procedures. Various attempts have been made to improve the performance of HPLC detection by interfacing GC detectors to an LC system.

In recent years, papers have been published on flame ionization, photoionization, nitrogen–phosphorus, flame photometric and electron-capture detection (ECD) [1–4]. ECD has been used on-line with moving-wire systems [5] and with nebulizing [6] and vaporizing interfaces [7]. With a recent miniaturized version (with a 200 × 0.7 mm I.D. column) the detection limits for favour-

able electron-capturing compounds (chloroanilines) were of the order of 0.2–10 pg [8].

A chlorine-selective flame-based detector using the indium(I) chloride emission band at 360 nm was described by Folestad et al. [9] for microbore LC (20–70 μl/min). Under non-retaining conditions, the detection limit for 1,1,2-trichloroethane is 0.39 ng of injected compound, provided that quenching effects by organic modifiers are avoided and pure water is used as the mobile phase. The use of electrolytic conductivity detection (ELCD) with an instrument designed for GC has the advantage of low sensitivity for non-halogenated interferents. This means that most of the sample clean-up associated with other types of detectors can be eliminated.

In the ideal case, the detector response is proportional to the chlorine content of a compound; this offers the possibility of quantitative determination without calibration for each compound in question.

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Basic research in this field was carried out by Shepherd et al. [10] using a segmented stream splitter to reduce the eluent flow reaching the detector. The development of miniaturized HPLC allows the introduction of the entire effluent into the GC detector.

The performance of the HPLC–ELCD system was investigated by varying parameters such as eluent flow-rate, interface position, reaction gas flow and reaction temperature. Various applications of HPLC–ELCD under normal-phase conditions are demonstrated and discussed.

2. Experimental

2.1. Apparatus

HPLC system

A syringe pump (LDC/Milton Roy) was used for delivering pulse-free flow-rates in the range 1–500 μl/min. The narrow-bore column employed (300 × 1 mm I.D.) was packed with 5-μm NH$_2$-Nucleosil (Grom, Herrenberg, Germany). Injections were made with a Rheodyne Model 7010 injection valve equipped with a 2 or 4-μl external sample loop.

Detector

The detection system consisted of a Model ROK 3/30 horizontal tube furnace (Heraeus, Hanau, Germany) including a quartz pyrolysis tube (350 × 1 mm I.D.), a Tracor Model 700A differential conductivity cell and a Tracor Model 700 control unit (Techmation, Düsseldorf, Germany). Data analysis was performed with a Shimadzu, C-R3A integrator.

Interface

The design of the laboratory-made interface is shown in the inset in Fig. 1. The front part of the pyrolysis tube has an extended inner diameter (3.5 mm I.D.). The stainless-steel capillary (20 cm × 0.1 mm I.D.) from the analytical column enters the tube through a Swagelok tee-piece (1/4 in.) and stops where the pyrolysis tube begins to narrow. The capillary end has a hand-filed tip so that the resulting orifice acts as a restrictor for a liquid stream down to 10–20 μl/min. Thus, the column effluent can be nebulized for supporting the vaporization process. The
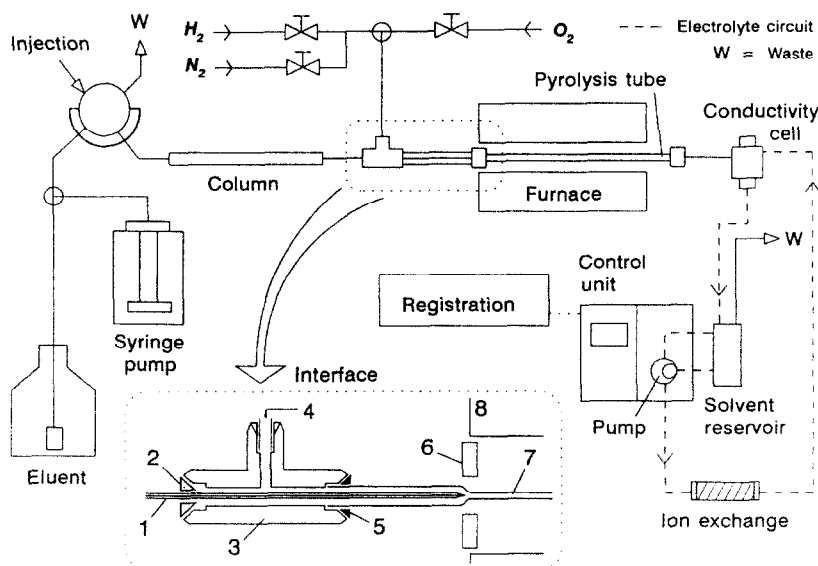

Fig. 1. Schematic diagram of the HPLC–ELCD system. Interface details: 1 = LC capillary; 2 = PTFE ferrule; 3 = tee-piece; 4 = reaction gas inlet; 5 = graphite ferrule; 6 = ceramic ring; 7 = quartz tube; 8 = furnace.

performance of the interfaced ELCD instrument was compared with that of a variable-wavelength UV detector (Model 575; Applied Biosystems, Weiterstadt, Germany).

2.2. Chemicals

The solvents used were of analytical-reagent grade from Merck (Darmstadt, Germany) and Baker (Deventer, Netherlands). They were used as received, except for *n*-pentane and *n*-hexane, which were purified by refluxing over a dispersion of 45% sodium in paraffin (Fluka, Buchs, Switzerland) and subsequent distillation [11]. Tetrachloromethane and 1,1,1-trichloroethane (analytical-reagent grade) were obtained from Merck; all other compounds used as solutes were analytical reagent grade products from Fluka, Riedel-de Haën (Seelze, Germany), Aldrich (Steinheim, Germany) and Polyscience (Niles, IL, USA).

High-purity hydrogen (99.999%) was used as the reaction gas. All solvents used as eluents were previously degassed under vacuum.

3. Results and discussion

The physical nature, in particular the detector transparency and evaporation properties, of the mobile phase and the volume of the eluent transferred into the detection unit are key factors for successful LC interfacing. The on-line-coupling of a GC detector to a liquid chromatograph requires continuous effluent vaporization. The constancy of this process has a direct influence on the detection limits. Favourable evaporation conditions, however, should agree with the conditions required by the chromatographic process and with the parameters demanded for the detector operation.

3.1. HPLC solvent and flow-rate

In spite of the detector selectivity, the solvent flow, which has to be evaporated, produces a background noise depending on the solvent used, the impurities and the flow-rate. The

combustion products of the eluent act as interfering compounds, which are constantly present in the detector and can increase the limit of detection for halogenated compounds.

To compare the interfering properties of possible eluents, solutions of tetrachloromethane in methanol, acetonitrile and *n*-pentane were prepared. The solutions were directly injected (4 μl in each instance) into the detector via a GC injection port and a fused-silica capillary (250 × 0.53 mm I.D.) as transfer line, heated at 100°C. Hydrogen acted as the carrier gas (50 ml/min) and the reaction gas (150 ml/min). This resulted in a higher sensitivity with the alkane as solvent, especially where lower concentrations were concerned (Fig. 2). It is also seen that a non-linear relationship exists with methanol and acetonitrile as solvents at a concentration range that is more than two orders of magnitude smaller than that which was investigated by Shepherd et al. [10].

The baseline noise with a continuous solvent flow increases with increase in flow-rate. The best results were observed with alkanes as eluents. To achieve the highest signal-to-noise ratios, the flow-rates, or at least the fraction of the LC effluent reaching the detector, should not exceed 60–80 μl/min, as can be seen from Table 1.

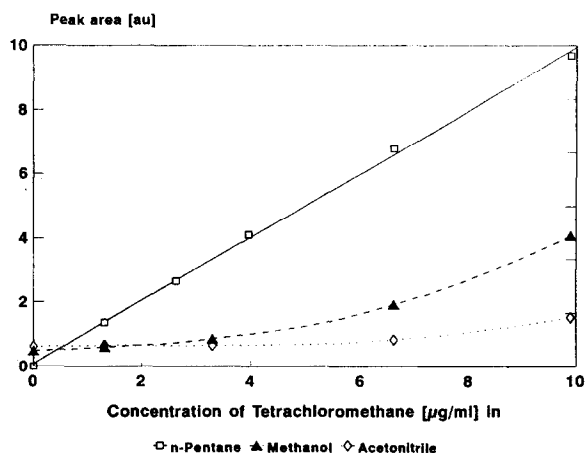A further disadvantage of increased flow-rates

Fig. 2. Influence of the solvent on the chlorine sensitivity. For conditions, see text.

Table 1
Influence of the eluent flow-rate on the signal-to-noise ratio

Eluent flow-rate (μl/min)	Signal-to-noise ratio	Eluent flow-rate (μl/min)	Signal-to-noise ratio
10	74	90	51
30	77	110	36
50	75	130	32
70	60	150	28

Eluent, n-pentane; reaction temperature, 1000°C; hydrogen flow-rate, 200 ml/min; injections (without separation column), 4 ng of tetrachloroethylene.

is a greater deposition of carbon in the furnace tube. The extent of this deposition depends on the eluent used and its carbon content. A flow-rate of 40 μl/min of n-hexane gives a distinct carbon deposition in the furnace tube after only 20 min, whereas no carbon is found with methanol as solvent, even after 40 min.

To decrease the detector load, a miniaturized LC system with a column of 1 mm I.D. was employed. Typical flow-rates of 5–50 μl/min allow the entire column effluent to be fed into the detector.

The increase in volume that occurs on converting the liquid eluent into vapour is, compared with the reaction gas flow, negligible at these flow-rates. In spite of greater carbon deposition, further investigations were confined to normal-phase chromatography with alkanes as solvents, because of a more sensitive determination.

Moreover, cleaning of the reaction tube by burning the carbon deposits can be carried out easily by changing the reaction gas to oxygen for 30 min when the eluent flow is turned off. The conductivity cell should be removed for this operation. Although no effect on sensitivity was observed over an operating period of 7 days (with an average of 2–4 h operation daily), this cleaning procedure was performed every 2 days.

Great variations in solvent purity were observed, although the same brands and grades were employed. Whereas single charges of n-hexane or n-pentane could be used as received from the suppliers, most of them show high noise levels (when used as eluents) and give peaks

(when injected as solvents). Sensitive and reproducible results could be obtained after purification of the alkanes in the above-described manner.

3.2. Hydrogen flow-rate

According to manufacturers' recommendations, operation in the halogen mode requires a hydrogen-flow-rate of 50 ml/min. This adjustment cannot be applied for the LC-coupled system, because the eluent has to react additionally. The theoretical consumption of hydrogen, assuming that methane is produced exclusively, which is a coarse approach, because other reaction products are also formed, is 43 ml/min at an n-hexane eluent flow-rate of 50 μl/min. This excess demand should be considered to achieve complete decomposition of the analyte.

In fact, the effect of an insufficient supply of reaction gas is observed. This is particularly apparent with aromatic chlorine compounds with a high carbon content. Distinctly diminished signals of di- and trichlorobenzenes are obtained at flow-rates below 80 ml/min, whereas varying the hydrogen flow-rate between 10 and 100 ml/min has no observable effect on the sensitivity for tetrachloromethane and tetrachloroethylene.

Further, as a result of a more efficient decomposition, increased hydrogen flow-rates (200 ml/min as compared with 75 ml/min at an n-pentane eluent flow-rate of 50 μ/min) decrease both the baseline noise and the carbon deposition in the pyrolysis tube. Above 300 ml/min, however, increased hydrogen flow-rates decrease the residence time in the reaction tube, which results in diminished signals. Hence a hydrogen flow-rate of 200 ml/min was routinely employed.

3.3. Reaction temperature

The efficiency of the thermal fragmentation also depends on the reaction temperature. Fig. 3 shows the temperature profiles of the response for three chlorinated compounds at an eluent flow-rate of 20 μl/min. With increasing furnace temperature, the detector response increases to a maximum. Unlike in its GC application, higher
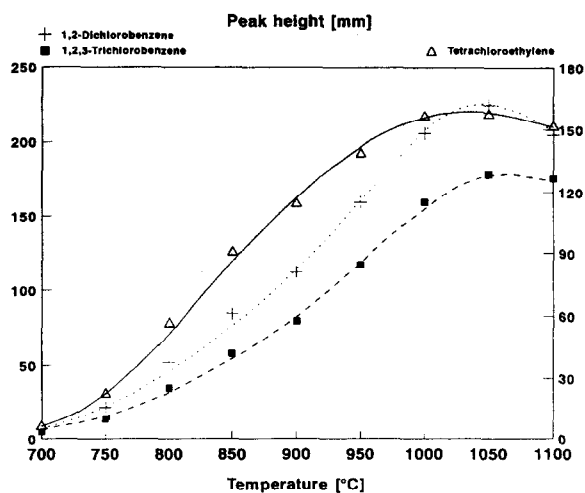
Fig. 3. Effect of reaction temperature on detector response.

furnace temperatures are required to obtain the maximum response. Further, because of the higher dissociation energy of the aromatic C–Cl bonds, the temperature must be sufficiently high to ensure that there is no difference in the response to aliphatic and aromatic compounds. Discriminating effects between the two groups are eliminated at a furnace temperature of 1050°C. In consideration of the working life of the furnace, however, a temperature of 1000°C was chosen for most experiments.

3.4. Conductivity solvent

The flow-rate of the solvent determines the concentration of the absorbed ions. Thus the detector response decreases with increasing flow-rate. Occasional carbon deposits in the conductivity cell may cause flow changes. To minimize variations in sensitivity, the correct volume flow, set at 0.6 ml/min, was checked daily. Undiluted ethanol was used as a conductivity solvent instead of alcohol–water mixtures, which tend to change their composition owing to gradual evaporation. In spite of the on-line coupled modification, the electrolyte is continuously circulated through the ion-exchange resin (Fig. 1) without any deterioration in sensitivity even after several weeks. Replacement of the resin

and solvent is necessary when the background noise increases significantly.

3.5. Selectivity

As specific detector, the ELCD instrument responds only to compounds that contain elements for which it is tuned. The selectivity is determined by the products formed in the furnace tube. Under reductive conditions (in the halogen mode hydrogen is used as reaction gas) strong acids are produced by the decomposition of organic halogen compounds. The low response of interfering compounds is due to poor solubility or low ionization of their pyrolysis products in the conductivity solvent. In spite of the selective properties of the detector, a large excess of interfering compounds can lead to systematic errors. To quantify the selectivity under coupling conditions, the chlorine response is compared with the responses to other heteroatomic compounds, which produce corresponding hydrogen compounds such as NH_3, H_2S and H_2O.

Solutions of these compounds in n-pentane (10 μl/ml) were injected into the solvent stream (40 μl/min). The separation column was removed for this operation. The response data shown in Fig. 4 are expressed in terms of peak areas related to the amount injected. Under the described conditions, a selectivity of 10^4–10^6 for organic-bound chlorine relative to the investigated compounds is achieved.

3.6. Interface

The interface must provide for an efficient transfer of analyte molecules from the LC outlet into the detector, while the contribution to band broadening must be minimized.

The most important parameters influencing the interface performance are the temperature and the shape of the interface. As far as the geometry is concerned, the interface must project into an opening of 1.5 mm because of the pyrolysis tube diameter. Further, the interface construction includes the reaction gas feed implied by the detection method. A possible later
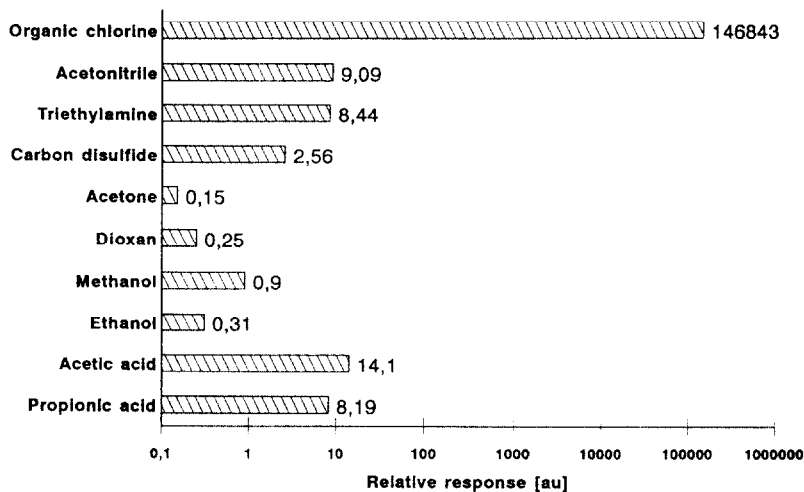
Fig. 4. Relative detector responses to various heteroatomic compounds.

supply would cause an additional band broadening, or a make-up gas stream as in the GC mode. The position of the liquid–vapour transition is determined by the interface temperature. It can be regulated by varying the position of the interface with respect to the heating zone of the furnace.

Different possibilities of solvent evaporation can be discussed. At low temperatures, the liquid flows until the capillary end and evaporates after leaving the capillary. In the case of a non-restricting orifice, this happens more as a result of the reaction gas stream passing by and would be a completely insufficient transfer for non-volatile solutes. At sufficiently high temperatures, the interface would be used under conditions of inside-capillary evaporation. With extremely volatile solvents (e.g., n-pentane) however, the "solvent concurrent evaporation" effect is risked with this operation. In this instance, the solvent evaporates at the liquid front, whereas high-boiling compounds are retained at the inner wall of the capillary.

All these effects are indicated when operating the interface without eluent nebulization. The measurements were made at various interface positions with solutes of different volatility. For high temperatures (>400°C), the stainless-steel

capillary projected 30 mm into the heating zone of the furnace. To avoid inside-capillary evaporation, the capillary tip was set at a distance of 10 mm from the furnace front. Exact temperatures at the capillary orifice inside the interface cannot be ascertained because of the cooling reaction gas jacket. This resulted in small and broadened peaks for hexachlorobenzene, whereas no band-broadening effects were observed for more volatile compounds (perchloroethylene or 1,2 dichlorobenzene). For 2,2',3,4,4',5,5'-heptachlorobiphenyl, no signal could be obtained with the crude capillary outlet under the various temperature conditions.

In contrast, high-pressure nebulization of the eluent permits the transfer even of the less volatile investigated compounds without evident band broadening; note peaks 2 and 4 in Fig. 5. The contribution of the interface to band broadening is identical with that which can be obtained with a UV detector equipped with a low-volume detector cell (0.5 μl) under identical chromatographic conditions, including the length and inner diameter of all connecting tubings. A liquid jet transports the solute molecules into zones of sufficiently high temperature. In order to achieve a steeper temperature gradient, the furnace aperture is diminished by a ceramic ring,
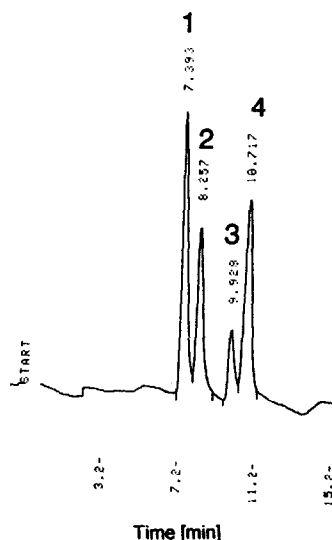
Fig. 5. ELCD chromatogram of an organochlorine standard mixture; Column, 5-μm Nucleosil NH₂ (300 × 1 mm I.D.); eluent, n-pentane (30 μl/min); hydrogen flow-rate, 200 ml/min; furnace temperature, 1000°C. Peaks: 1 = tetrachloroethylene (4 ng); 2 = hexachlorobenzene (4 ng); 3 = 1,2-dichlorobenzene (4 ng); 4 = 2,2',3,4,4',5,5'-heptachlorobiphenyl (5 ng).
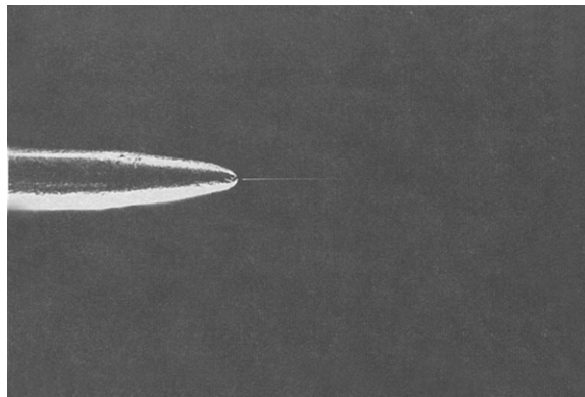

Fig. 6. Photograph of the nebulizing capillary tip and the liquid jet produced at an n-pentane flow-rate of 30 μl/min. For dimensions, see capillary diameter of 1.6 mm. The furnace and the quartz tube are removed.

which allows the capillary tip to reach up to the furnace front (Fig. 1).

The condition for a jet disintegrating into a spray of droplets can be evaluated by the equation [12]

$$d < \sqrt[3]{\frac{2\rho F^2}{\pi^2 \sigma}}$$

where d is the orifice diameter, F is the solvent flow-rate, ρ is the density and σ the surface tension of the liquid. Thus, the prepared stainless-steel capillary produces a continuous jet at an n-pentane flow-rate of 30 μl/min if the orifice of the capillary end has a diameter of 13 μm or less. This calculation can be verified by examination of a cut-off of the capillary tip using a scanning electron microscope: A photograph of the liquid jet at an n-pentane flow-rate of 30 μl/min is shown in Fig. 6.

Possible pneumatic nebulization with hydro-gen as nebulizer gas would require such high gas flow-rates that they would not be compatible with operation of the conductivity cell.

3.7. Detector performance and application

The limits of detection for some selected compounds are summarized in Table 2. In order to determine the chlorine response under coupled conditions, the sensitivity for the investigated compounds, obtained from the slope of the calibration graphs, is divided by the chlorine content. The relative values in Table 2 show the linear response to the content of chlorine in the molecule. Assuming a normal peak width of ca. 35s, the chlorine sensitivity found is in the 2–3 pg/s range, which is also specified in GC use.

The present set-up is suitable for analysing solid or aqueous environmental samples, subsequent to enrichment, using liquid–liquid or liquid–solid extraction. The organic extracts can be directly injected into the system. The advantage of the specific detection, which does not exist with other HPLC detectors, is shown in Fig. 7, which compares the ELCD and UV traces for a contaminated soil extract; the characterization of the signals obtained with

Table 2
Characteristics of some selected chlorinated organic compounds

Compound	Limit of detection (3s) (pg)	Relative standard deviation ($n = 4$) (%)	Chlorine content (%)	Relative chlorine sensitivity
1,3-Dichlorobenzene	205	2.8	48	1.00[a]
1,2-Dichlorobenzene	257	3.8	48	1.07
1,2,3-Trichlorobenzene	209	3.2	59	0.97
Hexachloroethane	58	1.0	90	0.96

[a] Defined.

ELCD as 1,2- and 1,3-dichlorobenzene was achieved by comparison with reference data (GC–MS analysis).
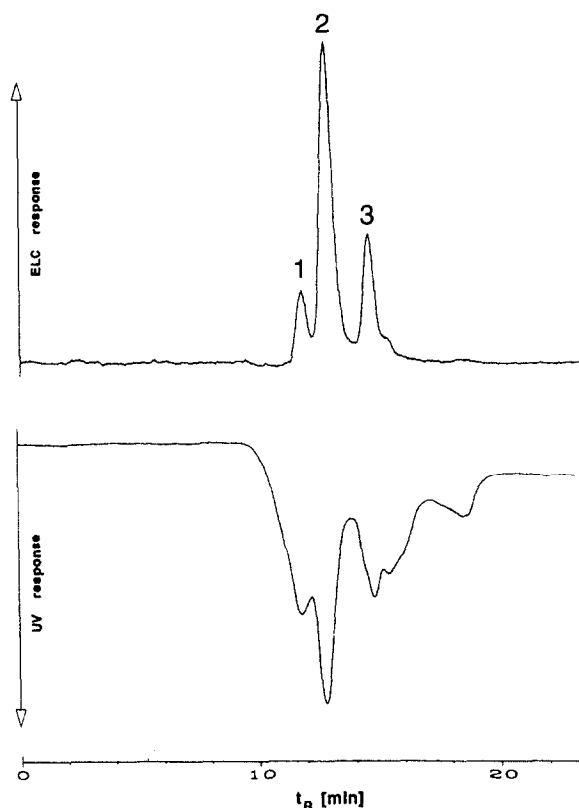

Fig. 7. LC–UV and LC–ELCD traces for a soil extract. Sample, 7.5 g soil; solvent, 5 ml of *n*-hexane; extraction period, 1 h; UV detection at 205 nm. Peaks: 1 = unidentified halogenated aliphatic; 2 = 1,3-dichlorobenzene; 3 = 1,2-dichlorobenzene.

4. Conclusions

The on-line coupling of a electrolytic conductivity detector to a miniaturized LC system has been successfully accomplished. The interface is based on nebulizing the total column effluent, while the contribution to band broadening is negligible. The minimum detectable amounts of chlorine (52–123 pg) are about 1000 times lower than those found in earlier studies.

The described HPLC–ELCD interfacing offers a very useful extension to the available range of the LC detectors and has its advantage in areas where thermal instability and low volatility make analysis by GC difficult. Compared with ECD, ELCD has the advantage of a direct proportionality between the response and the chlorine content of a compound. This can also be an interesting aspect for application as an extended parameter of extractable organic halogen compounds (EOX), with the possibility of sample characterization.

Further investigations on chromatographic optimization (shortening of extra-column tubings, use of polar modifiers and phase separators for coupling to reversed-phase chromatography) should improve the chromatographic resolution and increase the possibilities of identification and application.

5. Acknowledgement

6. References

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