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Note

Application of the electron-capture detector in liquid chromatography

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In recent years, high-performance column liquid chromatography (LC) has emerged as a method equivalent in performance to gas chromatography (GC). Today, these techniques are seen as supplementary rather than competitive, each having specific advantages and drawbacks, and each having preferred field(s) of application. A particular drawback in LC is the lack of detectors that can match the sensitivity of GC detectors. Currently, UV absorption detectors are probably the most widely used in LC, but fluorimetric and electrochemical detectors are increasingly used. In 1971, Nota and Palombari¹ designed an electron-capture detector (ECD) for LC; in 1974 an improved form was described by Willmott and Dolphin². The latter detector is now manufactured by Pye Unicam (Cambridge, Great Britain) and sold by Philips (Eindhoven, The Netherlands). Surprisingly, however, very few data on the use of this seemingly attractive detector system have been published³⁻⁵.

In this paper, the potential of the LC-ECD system and some of the inherent problems are discussed.

MATERIALS AND METHODS

Liquid chromatography was carried out using a Siemens S100 liquid chromatograph equipped with a Valco six-port injection valve (50- μ l loop) and a Zeiss PM2 DLC UV detector; for the determination of UV detection limits, a Perkin-Elmer LC-55 was used instead. The separation column was a 25 cm \times 3 mm I.D. stainless-steel tube pre-packed with 5- μ m LiChrosorb SI 60 silica gel (Merck, Darmstadt, G.F.R.). As the mobile phase for LC, *n*-hexane (ChromAR and Nanograde, Mallinckrodt, St. Louis, Mo., U.S.A.; Distol, Fisons, Loughborough, Great Britain; Resi-Analyzed, Baker, Phillipsburg, N.J., U.S.A.) and 2,2,4-trimethylpentane (isooctane) (Nanograde, Mallinckrodt; Analyzed, Baker) were used; they were dried over molecular sieve 5A. The system was thermostated at $27 \pm 1^\circ$.

The EC detector was coupled on-line with the UV detector. From the latter, the eluate passed into a stainless-steel capillary transfer tube enclosed in an oven, the temperature of which was such that complete vaporization of the liquid was ensured. The vapours were then passed into a ⁶³Ni ECD (Pye Unicam) mounted within the same oven. A nitrogen purge swept the vapour through the detector and into a coil of stainless-steel tubing where it was condensed and collected as a liquid.

In the present study, the oven temperature was normally kept at its maximal value (350°) and so was the flow-rate of purge gas (30 ml·min⁻¹). No special precaution was taken to remove trace amounts of oxygen from the nitrogen purge (A-28, maximal oxygen content 3 ppm; A.G.A., Amsterdam, The Netherlands). ECD and UV chromatograms were recorded simultaneously by means of a dual-pen recorder. Using decachlorobiphenyl (DCB) as a model compound, a band broadening of $\sigma_t = 4$ sec was calculated for the ECD.

The polychlorobiphenyl (PCB) samples investigated included the Aroclor series (1221–1268) produced by Monsanto (St. Louis, Mo., U.S.A.); as is well known, the last two digits of the four-digit number indicate the weight per cent of chlorine. The more recently introduced Aroclor 1016 contains 41% (w/w) of chlorine. The polychloronaphthalene (PCN) samples studied were Halowax 1031, 1001, 1013 and 1051 (Koppers, Pittsburgh, Pa., U.S.A.), which contain *ca.* 22, 50, 56 and 70% (w/w) of chlorine, respectively. DCB was purchased from Aldrich Europe (Beers, Belgium). All other chemicals were of normal analytical-reagent grade quality.

RESULTS AND DISCUSSION

Solvents

During the initial stages of our research, it became apparent that none of the brands and grades of *n*-hexane or isooctane tested, if used as received from the suppliers, was sufficiently pure for uninterrupted use of the EC detector for a prolonged period of time to be possible. Occasionally, with a fresh bottle of solvent, satisfactory results (*i.e.*, low noise levels and hence low backing-off levels) were obtained for several days. However, frequently the performance would suddenly deteriorate overnight or (although unfortunately only seldom) improve. Even when using a number of bottles from the same batch, consistent results could not be obtained. Consequently, special attention was devoted to the removal of electron-absorbing contaminants from the solvents used as the mobile phase. Details of two promising clean-up procedures were kindly provided by Mr. H. L. Louwse (Philips, Eindhoven, The Netherlands): (1) a mixture of 1 l of solvent, 10 g of a sodium-lead alloy (10% Na) and 1 ml of propanol-2 is refluxed for 2–3 h, then the purified solvent is distilled; (2) a 1-in. thick disk of a 45% dispersion of finely divided ($d_p \approx 10 \mu\text{m}$) sodium metal in solid paraffin (Fluka, Buchs, Switzerland) is added to 1 l of solvent and, after refluxing for 1 h, the solvent is distilled.

With the former procedure, variable results were obtained and the loss of solvent often amounted to about 30%. The latter treatment, however, was highly successful with all six types of *n*-hexane and isooctane specified above; usually over 90% of the solvent was recovered. As a severe test, the procedure was used to purify waste *n*-hexane from clean-up and extraction of environmental samples containing PCBs. The dramatic improvement in the quality of the solvent is evident from Fig. 1. In addition, it is interesting that the quality of another sample of purified *n*-hexane did not change significantly on storage for 3 months.

Typical conditions that could now be maintained over a prolonged period of time were (at a flow-rate of *n*-hexane of 1.4 ml·min⁻¹): d.c., 40–45; attenuator, $\times 64$ or $\times 128$; peak-to-peak noise, 3–4% (see, for example, Fig. 2).

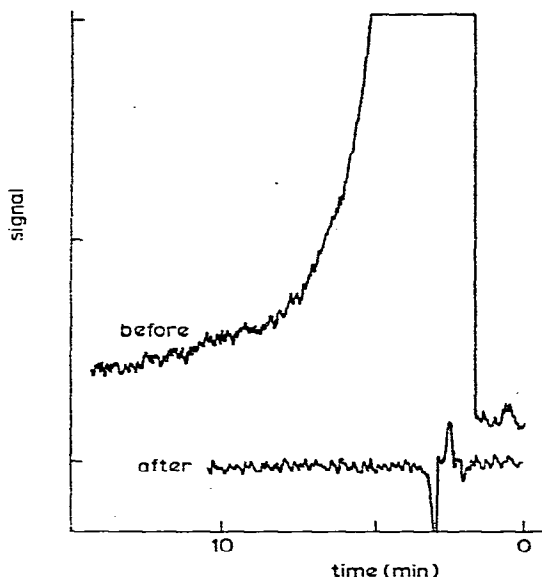


Fig. 1. LC-ECD chromatograms of waste *n*-hexane from clean-up and extraction of environmental samples before and after treatment with a dispersion of finely divided sodium metal in solid paraffin. System: silica gel-dry *n*-hexane.

Detection limits

Table I gives the minimum detectable amount (MDA) at a signal-to-noise ratio of 2:1 of several organochlorine pesticides and DCB using the ECD system. As a means of comparison, some data on MDAs for UV detection have been included. These are of the expected order of magnitude, the MDA often being stated to vary from about 10^{-8} to 10^{-10} g for the logarithm of the molar extinction coefficient ($l \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$) at the wavelength of maximum absorption ($\log \epsilon_{\text{max}}$) increasing from *ca.* 3 to 5. As regards the ECD, all of the compounds considered display MDA values in the range 10^{-10} – 10^{-11} g. The superiority of electron-capture over UV detection appears to be at least partly determined by the molar extinction coefficients of the various compounds tested. In other words, one should realize that the weakly UV-

TABLE I

MDA VALUES AND RELATED CHARACTERISTICS OF A NUMBER OF ORGANOCHLORINE PESTICIDES AND DCB FOR ELECTRON-CAPTURE AND UV DETECTION

Capacity ratio $k' = (t_R - t_0)/t_0$; $N_{\text{column}} = \text{ca. } 3000$.

Compound	k'_{LC}	MDA_{ECD} (g)	MDA_{UV} (g)	$\log \epsilon_{\text{max}}$	λ_{max}
Aldrin	1.0	$1 \cdot 10^{-11}$		3.75	210
		$4 \cdot 10^{-11}$ *	$1 \cdot 10^{-8}$ *	3.40*	230*
DCB	0.5	$1 \cdot 10^{-11}$	$2 \cdot 10^{-10}$	5.05	215
<i>p,p'</i> -DDD	17.5	$1 \cdot 10^{-10}$		4.50	202
<i>o,p'</i> -DDE	4.5	$5 \cdot 10^{-11}$		4.65	197
<i>o,p'</i> -DDT	4.5	$7 \cdot 10^{-11}$	$1 \cdot 10^{-9}$	4.65	201
<i>p,p'</i> -DDT	6.0	$5 \cdot 10^{-11}$	$1 \cdot 10^{-9}$	4.65	201
Heptachlor	2.5	$3 \cdot 10^{-11}$		4.00	196

* Data taken from ref. 2.

absorbing aldrin (used as test compound by Willmott and Dolphin²) is a particularly favourable example from the point of view of the ECD principle.

As an application, *p,p'*-DDT and *o,p'*-DDE were added to a sample of Dutch river water to obtain final concentrations of 0.03 and 0.10 ppb^{*}, respectively. A 500-ml volume of the spiked sample was extracted with 25 ml of *n*-hexane and the extract evaporated to a volume of 5 ml. Chromatograms of extracts of a non-spiked and a spiked water sample are shown in Fig. 2. Obviously, with a slightly more efficient concentration procedure (with evaporation to about 1 ml) and/or when using larger injection volumes (200–300 μ l), detection limits of 1–10 ppt can be achieved.

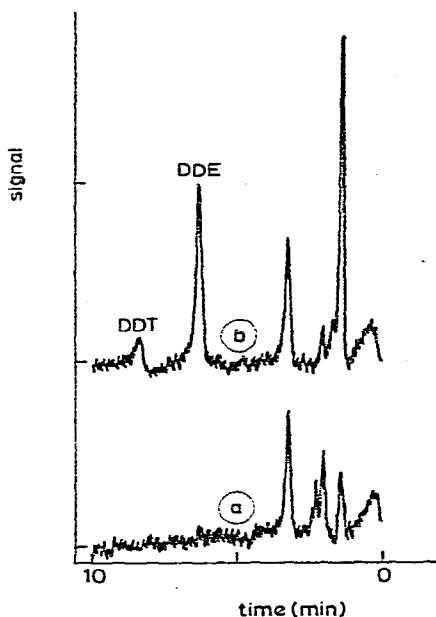


Fig. 2. LC-ECD chromatograms of *n*-hexane extract of (a) non-spiked river-water sample and (b) sample spiked with 0.03 ppb of *p,p'*-DDT and 0.10 ppb of *o,p'*-DDE. System: silica gel-dry *n*-hexane; flow-rate, 1.4 ml·min⁻¹. ECD: d.c., 40; attenuation, $\times 64$.

Pattern recognition

The PCBs occur in a variety of environmental samples. Identification and quantitation are often effected by comparing the peak pattern observed for the sample (extract) with that of commercially available PCB mixtures. In a paper on the GC analysis of a related class of compounds, the PCNs, Beland and Geer⁶ pointed out that GC with an ECD, in contrast with, e.g., GC with a flame-ionization detector, may give misleading values of the amounts of each individual PCN (PCB) present; whereas the response of the flame-ionization detector is relatively insensitive to the number of chlorine substituents, a less than 2-fold change occurring from mono- to tetrachloro-PCBs⁷, there is a very large increase in the EC detector response between mono- and octa(deca)chloro-PCNs (PCBs), most of this increase occurring in the

* Throughout this article, the American billion (10⁹) and trillion (10¹²) are meant.

mono- to trichloro range^{6,7}. For LC, the same situation may be thought to arise when comparing LC-ECD and LC-UV detector systems. Therefore, in the present study, chromatograms of a large series of PCB and PCN mixtures were run in the system silica gel (LiChrosorb SI 60)-dry *n*-hexane, which is well known^{8,9} to yield interesting peak profiles for these types of mixtures. Three chromatograms are shown in Fig. 3. From the complete set of data, two main conclusions can be drawn.

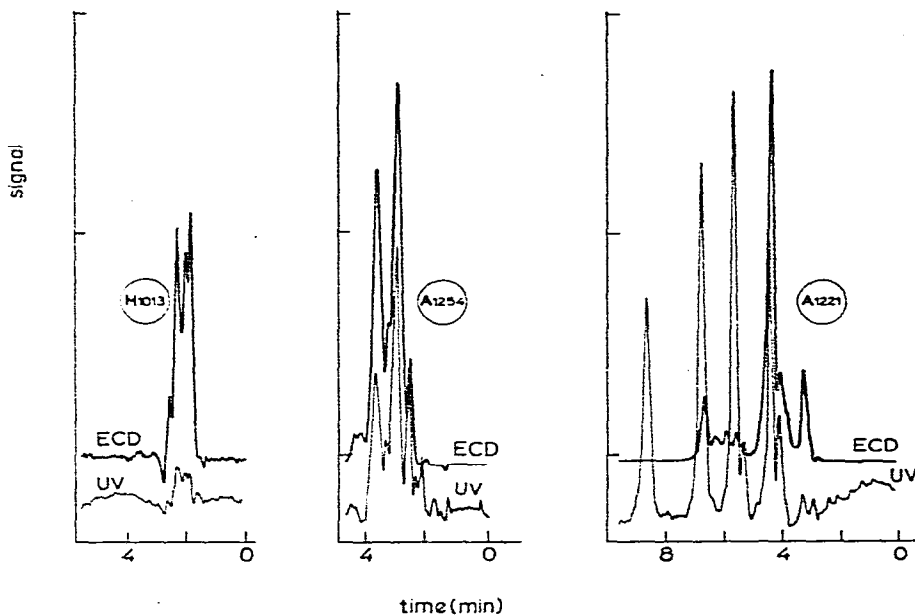


Fig. 3. Comparison of ECD and UV recordings of LC chromatograms of Aroclor 1221, Aroclor 1254 and Halowax 1013, run in the system silica gel-dry *n*-hexane (flow-rate $1.4 \text{ ml} \cdot \text{min}^{-1}$). ECD: d.c., 27; attenuation, $\times 1024$; UV detection at 246, 230 and 238 nm, respectively; a.u.f.s., 0.02 in all instances.

Firstly, the LC-ECD and LC-UV detector patterns are similar for all of the PCN mixtures investigated. With the Aroclors, the patterns are very similar for the more highly chlorinated biphenyls (1242-1268) and less so for Aroclor 1016, while all similarity is apparently lost with the low-chlorinated Aroclor 1221. With the latter mixture, special attention is drawn to the late-eluting major peak at $t_R \approx 8.5 \text{ min}$. This has been attributed⁸ to the non-halogenated parent compound biphenyl (12-13%, w/w)^{8,10}, which does not display favourable electron-capturing properties. The results obtained with the Aroclors can at least partly be explained by the fact that with increasing chlorine content the number of individual PCBs in the mixture rapidly increases, while the retention, and thus resolution, decreases. Consequently, differences in EC-UV detector response ratios for individual compounds, which certainly do exist^{7,8}, will be largely eliminated.

Secondly, using the most prominent peaks present in the patterns of the various chlorinated mixtures, a rough estimate was made of the gain in sensitivity that occurred on substituting the ECD for the UV detector. Calculations were made using chromatograms run under optimal conditions, which in some instances were

substantially different from those reported in the legend to Fig. 3, *e.g.*, with regard to the wavelength used in UV detection; note also the very high attenuation value with the ECD. With the Aroclors, the gain increases from 5–10-fold for Aroclors 1016 and 1221 to about 30-fold for Aroclor 1268. In the Halowax series, the results vary between 0.5 for Halowax 1031 and about 15 for Halowax 1051. Here, one should bear in mind that in both series the ECD response factors increase with increasing number of chlorine substituents. However, whereas $\log \epsilon_{\max}$ slowly rises (from 4.6 to 4.9) on going from Aroclor 1221 to Aroclor 1268, it decreases⁹ with increasing chlorine content in the Halowax series, *viz.*, from 5.0 to 4.7.

CONCLUSION

A rapid and inexpensive method for producing highly pure aliphatic hydrocarbon solvents, which can conveniently be used as mobile phases in LC-ECD systems, has been described. For, *e.g.*, chlorinated pesticides and highly chlorinated biphenyls and naphthalenes, such systems offer highly improved detection limits in comparison with analyses by means of LC with UV detection. The reduction in sensitivity compared with standard GC is only modest² and can be estimated to be about 10-fold (see, *e.g.*, refs. 12 and 13 for GC-ECD data). In actual analyses, the situation is even more favourable, as the use of much larger injection volumes in LC than in GC (typically 100 compared with 1 μ l) will largely offset the drawback of higher MDA values in LC. A disadvantage of LC-ECD compared with GC-ECD is that very high-boiling compounds, such as the tetradecachloroterphenyls, which still can conveniently be determined by means of GC, yield broad and severely tailing peaks in LC-ECD and therefore cannot be subjected to this type of analysis. In agreement with this, it was observed by us that with DCB, increasing the temperature

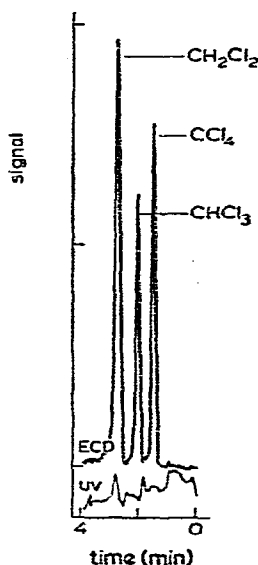


Fig. 4. Comparison of ECD and UV recordings of a liquid chromatogram of di-, tri- and tetrachloromethane run in the system silica gel-dry *n*-hexane (flow-rate 1.4 ml·min⁻¹). ECD: d.c., 34; attenuation, $\times 128$; UV, detection at 230 nm; a.u.f.s., 0.02.

from 320° to 350° doubled its peak height, while Willmott and Dolphin² reported that for the relatively low-boiling aldrin a suitable temperature range is 150–250°.

Clearly, examples that will serve to illustrate more dramatically the superiority of the ECD over the UV detection should be taken from classes of compounds such as the halogenated aliphatic hydrocarbons. Fig. 4 shows the efficient separation and detection of di-, tri- and tetrachloromethane, all of which display weak UV absorption, in the system silica gel–dry *n*-hexane, using the ECD. For these three compounds, MDAs of *ca.* 10⁻¹⁰ g were determined.

REFERENCES

- 1 G. Nota and R. Palombari, *J. Chromatogr.*, 62 (1971) 153.
- 2 F. W. Willmott and R. J. Dolphin, *J. Chromatogr. Sci.*, 12 (1974) 695.
- 3 A. T. Chamberlain and J. S. Marlow, *J. Chromatogr. Sci.*, 15 (1977) 29.
- 4 R. J. Dolphin and F. W. Willmott, *J. Chromatogr.*, 149 (1978) 161.
- 5 R. J. Dolphin, F. W. Willmott, A. D. Mills and L. P. J. Hoogveen, *J. Chromatogr.*, 122 (1976) 259.
- 6 F. A. Beland and R. D. Geer, *J. Chromatogr.*, 84 (1973) 59.
- 7 O. Hutzinger, S. Safe and V. Zitko, *The Chemistry of PCBs*, CRC Press, Cleveland, Ohio, 1974, Ch. 12.
- 8 U. A. Th. Brinkman, J. W. F. L. Seetz and H. G. M. Reymer, *J. Chromatogr.*, 116 (1976) 353.
- 9 U. A. Th. Brinkman, A. de Kok, H. G. M. Reymer and G. de Vries, *J. Chromatogr.*, 129 (1976) 193.
- 10 L. S. Kaminski and M. J. Fasco, *J. Chromatogr.*, 155 (1978) 363.
- 11 U. A. Th. Brinkman, A. de Kok, G. de Vries and H. G. M. Reymer, *J. Chromatogr.*, 128 (1976) 101.
- 12 B. Compton, *Progr. Anal. Chem.*, 5 (1973) 133.
- 13 L. Fishbein, *Chromatography of Environmental Hazards*, Vol. 2, Elsevier, Amsterdam, 1973, p. 264.