*Journal of Chromatography*, 394 (1987) 65–76
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 423

# COMPARISON BETWEEN POSITIVE, NEGATIVE AND CHLORIDE-ENHANCED NEGATIVE CHEMICAL IONIZATION OF ORGANOPHOSPHORUS PESTICIDES IN ON-LINE LIQUID CHROMATOGRAPHY–MASS SPECTROMETRY

D. BARCELÓ, F. A. MARIS*, R. B. GEERDINK*, R. W. FREI, G. J. DE JONG and U. A. Th. BRINKMAN

*Section of Environmental Chemistry, Department of Analytical Chemistry, Free University, De Boelelaan 1083, 1081 HV Amsterdam (The Netherlands)*

---

## SUMMARY

Positive and negative chemical ionization (PCI and NCI, respectively) have been used for the characterization of ten organophosphorus pesticides in on-line liquid chromatography–mass spectrometry (LC–MS). LC analyses were performed on a 20 cm × 0.7 mm I.D. $C_8$-bonded phase using acetonitrile–water (70:30) or acetonitrile–water–chloroacetonitrile (69:30:1) as eluent. With PCI, molecular weight information was obtained with both eluents. For NCI considerable differences in the spectra were found using the two eluents. Without chloroacetonitrile the spectra were dominated by the functional group fragment and with chloroacetonitrile the base peak was $[M - R]^-$ with R being methyl or ethyl, while the spectra further contained the functional group ions. Special emphasis was devoted to the occurrence of chloride attachment at different source temperatures. With several compounds the $[M + Cl]^-$ ion was formed and its relative intensity strongly increased when the source temperature decreased. With NCI the sensitivity was about one order of magnitude better than with PCI. This advantage was partly lost when 1% of chloroacetonitrile was used in the eluent; on the other hand, complementary structural information was obtained. As an application, the determination of three organophosphorus pesticides in sediment is reported.

---

## INTRODUCTION

The on-line combination of liquid chromatography and mass spectrometry (LC–MS) via the direct liquid introduction (DLI) of 10–20 μl/min of LC effluent into the source has been applied successfully by several workers in recent years[1–4]. Although fast atom bombardment[5] and electron impact[6] were occasionally used, chem-

---

* Present address: Institute for Inland Water Management and Wastewater Treatment, Ministry of Transport and Public Works, Postbox 17, 8200 AA Lelystad, The Netherlands.

0021-9673/87/$03.50 © 1987 Elsevier Science Publishers B.V.

ical ionization (CI)[7–10] is still the ionization mode most used in DLI LC–MS; it mainly provides molecular weight or functional group information.

As regards the trace level determination of organophosphorus pesticides such as diazinon, parathion-ethyl and coumaphos in food, and ronnel, coumaphos, dimethoate and azinphos-methyl in biological samples, it has been demonstrated for gas chromatography (GC)–MS[11–13] that it is advantageous to use chemical ionization (CI) rather than electron impact MS. Further, it has been reported[9] that, for the phosphorus pesticides, negative CI (NCI) is more sensitive than positive CI (PCI). This is attributed to the formation of more stable negative ions by the low-energy electrons in the MS source. Busch *et al.*[14] who used GC–MS with methane-enhanced negative ionization (MENI) reported that the sensitivity for organophosphorus pesticides with MENI is 10–25 times higher than in methane-enhanced PCI or electron impact MS.

Recently, Dougherty and Wander[15] have successfully applied PCI, NCI and chloride-attachment NCI to direct probe analysis. The applicability of on-line LC–MS with PCI and NCI was demonstrated by Parker and co-workers[8,9] for organophosphorus pesticides and the same group[10] was the first to use acetonitrile–water (79:20) containing 1% of chloroacetonitrile as eluent to achieve chloride-attachment NCI. Geerdink *et al.*[16] have shown the advantages of chloroacetonitrile as an additive in narrow-bore LC–MS, *e.g.*, for the determination of chlorophenols.

This work was aimed at expanding the general insight into the usefulness of PCI, NCI and chloride-enhanced negative ionization (CLENI) for the determination of organophosphorus compounds in on-line LC–MS.

## EXPERIMENTAL

### *Materials*

Water and acetonitrile were of HPLC grade (Baker, Deventer, The Netherlands) and were passed through a filter of 0.45 μm pore diameter before use. Analytical-reagent grade chloroacetonitrile was obtained from Fluka (Buchs, Switzerland) and paraoxon-methyl from Dr. Su. I. Ehrenstorfer (Augsburg, F.R.G.). Trichlorfon, parathion-methyl, ronnel, coumaphos, vamidothion, dimethoate, azinphos-methyl, azinphos-ethyl and carbophenothion were gifts from the Governmental Food Inspection Service (Alkmaar, The Netherlands).

### *Sample preparation*

Sample pre-treatment of a sediment from the lake Het Nieuwe Meer (Amsterdam, The Netherlands) was carried out via a method derived from a commonly used procedure for the pesticide residue analysis of soil and sediments[17]. A 30-g amount of sediment (wet weight) was spiked with the pesticides and refluxed with 200 ml of methanol–water (9:1) for 4 h in a Soxhlet apparatus. Subsequently, the solution was evaporated just to dryness on a rotary evaporator and the residue was dissolved in 2 ml of acetonitrile.

### *Chromatographic system*

A Gilson (Villiers-le-Bel, France) Model 302 high-pressure pump coupled with a laboratory-made membrane pulse damper provided stable eluent delivery. Samples were introduced with a laboratory-made microinjection valve with a 0.5-μl internal injection loop. For flow injection, the valve was directly coupled to the evaporation interface.

Glass-lined stainless-steel columns (GLT; 200 × 0.7 mm I.D.) (SGE, Melbourne, Australia) laboratory packed with 5 μm Hypersil ODS (Shandon, Runcorn, U.K.) were used. A Model PU 4025 UV detector equipped with a 1-μl micro-cell from Pye Unicam (Cambridge, U.K.) was used to record LC–UV chromatograms.

It should be pointed out that when an eluent containing 1% of chloroacetonitrile is used in LC–CLENI MS, it takes a long time before the chloroacetonitrile is completely removed from the chromatographic system so that it can be used again for LC–NCI (or PCI) MS.

### *Mass spectrometer*

A Finnigan (Sunnyvale, CA, U.S.A.) Model 4021 quadrupole mass spectrometer, with Varian (Palo Alto, CA, U.S.A..) Model M4 and HS2 diffusion pumps for the vacuum system, was used. A Data General Nova 4 (Data General, Westboro, MA, U.S.A.) was employed for data acquisition and processing.

Under the conditions used, the pressure in the ionization chamber was *ca.* 0.3 Torr and in the analyser $6 \cdot 10^{-5}$ Torr. The electron multiplier was operated at *ca.* 1170 V with a dynode voltage of 3 kV. The MS ion source temperature was varied between 180 and 300°C for CLENI and maintained at 300°C for PCI and NCI.

### *DLI interface*

The laboratory made interface has been described in detail previously[18]. It consists of a *ca.* 35-cm long outer stainless-steel jacket which fits into the solid sample probe of the MS instrument. The LC effluent enters the MS source through a fused-silica capillary (0.16 mm O.D. × 50 μm I.D.). This capillary is coaxial with a stainless-steel capillary (1/16 in. O.D. × 0.3 mm I.D.), and helium (at an inlet pressure of 1–2 bar) flows between both capillaries and into the MS source.

## RESULTS AND DISCUSSION

### *Mass spectra*

Ten organophosphorus pesticides were used as test compounds. They belong to five classes characterized by differences in the functional group (FG), as is indicated in Table I. Experiments were started by flow injection of the pesticides. The carrier stream was acetonitrile–water (70:30) without or with 1% of chloroacetonitrile, and measurements were carried out in the PCI and NCI modes. The results are summarized in Table II.

With PCI the $[M + H]^+$ ion was formed by all test compounds, and was the base peak for seven pesticides. In addition, for some of the pesticides an intense $[M-FG]^+$ ion was obtained. This fragment was the base peak for carbophenothion, azinphos-methyl and azinphos-ethyl; it corresponds to a resonance-stabilized species previously reported for direct-probe chemical ionization MS[19] and also by Singh *et al.*[13], who used methane as CI reagent gas in GC–MS. In contrast with our results, Voyksner and Haney[20] using a thermospray LC–MS interface for analysing, *e.g.*, dimethoate, azinphos-methyl and azinphos-ethyl, observed only $[M + H]^+$ and

TABLE I

ORGANOPHOSPHORUS PESTICIDES USED AS MODEL COMPOUNDS

| *Type and functional group (FG)* | *Compound* | *Mol. wt.* | *R* | *M − FG* |
|---|---|---|---|---|
| Phosphates, $(RO)_2PO_2$ | Paraoxon-methyl | 247 | $CH_3$ | $C_6H_6NO_2$ |
| Phosphonates, $(RO)_2PO$ | Trichlorfon | 256 | $CH_3$ | $C_2H_2Cl_3O$ |
| Phosphorothionates, $(RO)_2PSO$ | Parathion-methyl | 263 | $CH_3$ | $C_6H_4NO_2$ |
| | Ronnel | 320 | $CH_3$ | $C_6H_2Cl_3$ |
| | Coumaphos | 362 | $C_2H_5$ | $C_{10}H_6ClO_2$ |
| Phosphorothiolates, $(RO)_2POS$ | Vamidothion | 287 | $CH_3$ | $C_6H_{12}NOS$ |
| Phosphorodithioates, $(RO)_2PS_2$ | Dimethoate | 229 | $CH_3$ | $C_3H_6NO$ |
| | Azinphos-methyl | 317 | $CH_3$ | $C_8H_6N_3O$ |
| | Azinphos-ethyl | 345 | $C_2H_5$ | $C_8H_6N_3O$ |
| | Carbophenothion | 342 | $C_2H_5$ | $C_7H_6ClS$ |

$[M + NH_4]^+$ ions, but no other fragment which could provide structural information.

In the NCI mode (without chloroacetonitrile) the mass spectra were characterized by an intense $[FG]^-$ ion which was the base peak in all but four cases. Exceptions were trichlorfon, which has $[M - FG]^-$ as the base peak, and the phosphorothionates which have an aromatic ring bonded to the functional group. In the latter instance, the thiophenoxide ($-S-C_6H_5$) ion is the most abundant ion. It results from a rearrangement caused by electron capture which is followed by fragmentation with a transfer of the aromatic moiety from the oxygen to the sulphur atom. It is known that the thiophenoxide anion exhibits greater electron affinity than does phenoxide and, therefore, forms the more stable anion (refs. 11 and 12; see also refs. 8 and 14). As an example, the fragmentation scheme for parathion-methyl is shown in Fig. 1.

Further, the relative intensity of the $[M - R]^-$ cluster was lower than 4% in all instances and its intensity decreased with decreasing source temperature. Using a similar reagent gas and a source temperature of 140°C, Parker *et al.*[10] found a relative intensity of $[M - R]^-$ for dimethoate and carbophenothion of about 0.1%.

Manifest changes in the NCI spectra were observed on the addition of 1% of chloroacetonitrile. In this so-called chloride-enhanced negative ionization (CLENI) mode, the ionization process resulted in the loss of the R group from the pesticides to give generally $[M - R]^-$ as the base peak; for most pesticides a relatively intense $[FG]^-$ ion could also be observed. As an example, the changes in the relative intensity of the fragments of parathion-methyl after the addition of chloroacetonitrile have been included in Fig. 1. The relative intensities of 50 and 100% obtained by us for the $[M - R]^-$ ions of carbophenothion and dimethoate, respectively, are much higher than the values reported in the literature[15] for direct probe analysis of the same compounds, *e.g.*, 3 and 19%, respectively. Finally, chloride attachment was modest at a source temperature of 300°C in our work: for dimethoate, vamidothion, tri-

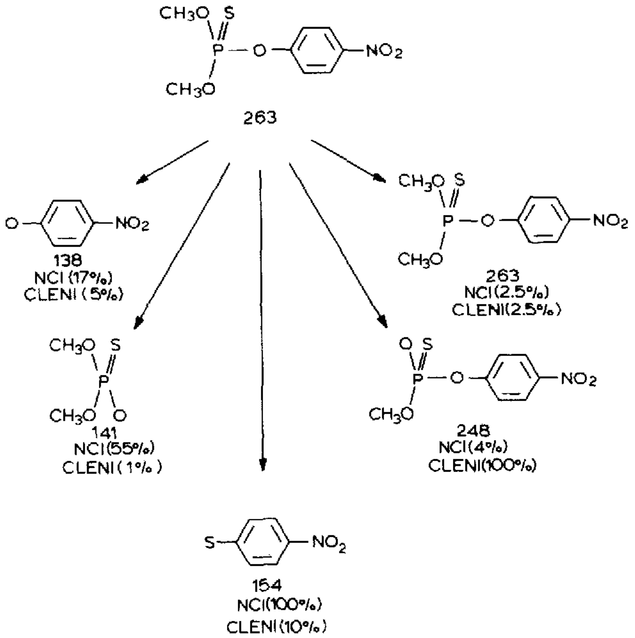

Fig. 1. Main fragments observed for parathion-methyl in NCI and CLENI modes. Conditions as in Fig. 2.

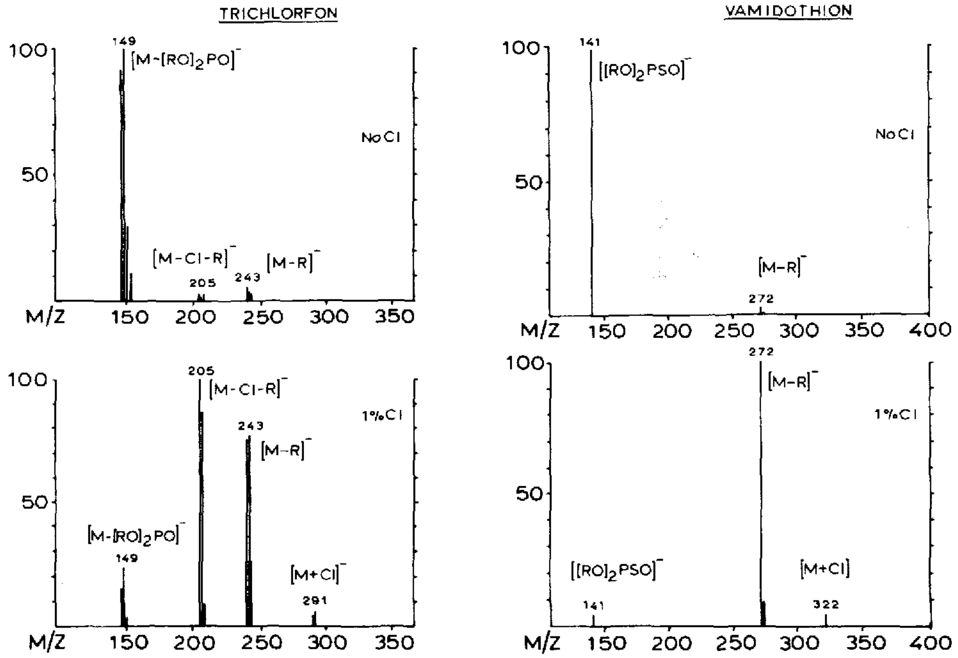

Fig. 2. Flow injection–NCI MS and –CLENI mass spectra of trichlorfon and vamidothion. Ion source temperature, 300°C; carrier stream, acetonitrile–water (70:30) for NCI or acetonitrile–water–chloroacetonitrile (69:30:1) for CLENI; flow-rate, 20 µl/min; scan time, 1 s.

TABLE II

*m/z* VALUES AND RELATIVE INTENSITY (% OF BASE PEAK) OF THE MAIN FRAGMENT IONS IN FLOW INJECTION–MS OF ORGANOPHOSPHORUS PESTICIDES IN THE PCI, NCI AND CLENI MODES AT AN ION SOURCE TEMPERATURE OF 300°C

Conditions: carrier stream, acetonitrile–water (70:30) with (CLENI) or without 1% of chloroacetonitrile, 20 μl/min.

| *Compound* | *PCI* | | *NCI* | | *CLENI* | | |
|---|---|---|---|---|---|---|---|
| | $[M-FG]^+$ | $[M+H]^+$ | $[FG]^-$ | $[M-R]^-$ | $[FG]^-$ | $[M-R]^-$ | $[M+Cl]^-$ |
| Paraoxon-methyl | | 248 (100) | 125 (100) | 232 (3) | (8) | (100) | 282 (−) |
| Trichlorfon | | 257 (100) | 147* (100) | 241 (2) | (22)* | (80) | 291 (8) |
| Parathion-methyl | | 264 (100) | 141 (55) | 248 (4) | (1) | (100) | 298 (−) |
| Ronnel | | 321 (100) | 141 (90) | 305 (−) | (37) | (100) | 355 (1) |
| Coumaphos | | 363 (100) | 169 (50) | 333 (−) | (22) | (100) | 397 (−) |
| Vamidothion | 146 (30) | 288 (100) | 141 (100) | 272 (2) | (5) | (100) | 322 (5) |
| Dimethoate | | 230 (60) | 157 (100) | 214 (2) | (15) | (100) | 264 (2) |
| Azinphos-methyl | 160 (100) | 318 (15) | 157 (100) | 302 (−) | (40) | (100) | 352 (−) |
| Azinphos-ethyl | 160 (100) | 346 (25) | 185 (100) | 316 (−) | (100) | (50) | 380 (−) |
| Carbophenothion | 157 (100) | 343 (100) | 185 (100) | 313 (−) | (100) | (50) | 377 (−) |

* Corresponds to $[M-FG]^-$.

chlorfon and ronnel the $[M + Cl]^-$ peak reached percentages of between 1 and 8%. In Fig. 2 the spectra of trichlorfon and vamidothion obtained in the NCI and CLENI modes are given.

In LC–PCI MS, the addition of chloroacetonitrile to the eluent changed neither the MS pattern nor the relative intensities of the various peaks.

### *Temperature dependence of chloride attachment in CLENI*

It has previously been reported[10,15,16,21] that the degree of chloride attachment is highly dependent on the ion source temperature. Decreasing the source temperature generally causes an increase of the $[M + Cl]^-$ ion intensity, both in direct probe analysis using dichloromethane as reagent gas[15] and with an LC–MS system using 1% of chloroacetonitrile[10,16]. In this study, 50 nl of a solution of *ca.* 1 mg/ml

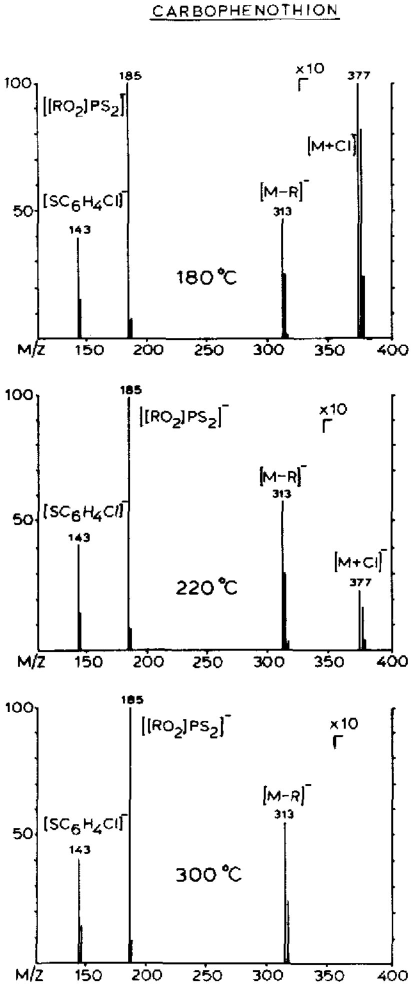

Fig. 3. CLENI mass spectra of carbophenothion at ion source temperatures of 180, 220 and 300°C. Other conditions as in Fig. 2.

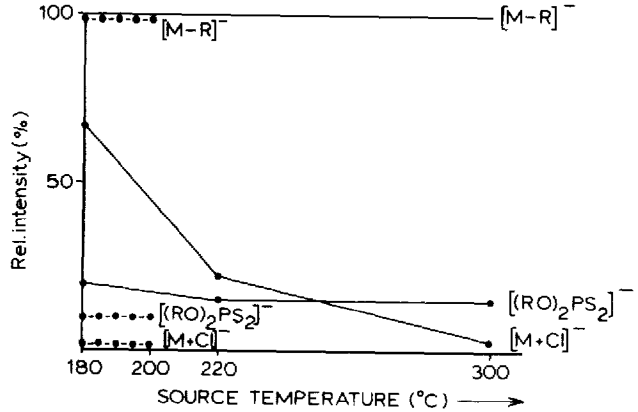

Fig. 4. Temperature study of selected ions from the CLENI mass spectra of dimethoate. Conditions as in Fig. 2. Comparison between the results of this work (solid lines) and those published in ref. 10 (broken lines).

of each component in acetonitrile–water–chloroacetonitrile (69:30:1) were introduced via flow injection into the mass spectrometer at a flow-rate of 20 μl/min; the source temperature was varied from 180 to 300°C. We observed that the degree of chloride attachment, *i.e.*, the $[M + Cl]^-$ ion intensity, distinctly increased as the source temperature decreased. As an illustration, the mass spectra of carbophenothion obtained at three different source temperatures are shown in Fig. 3. At a source temperature of 180°C chloride attachment was observed for six pesticides, reaching relative intensities of 100% for vamidothion and trichlorfon and of 67, 10, 7 and 2% for dimethoate, carbophenothion, ronnel and paraoxon-methyl, respectively. For the other fragments in the spectra the relative intensity remained the same on lowering the temperature.

In order to compare our results with those published in the literature, Fig. 4 shows the relative intensity of the major fragments for dimethoate as observed by Parker *et al.*[10] and in this work. The main difference is in the abundance of the $[M + Cl]^-$ ion. At a source temperature of 180°C, this difference amounts to about a factor of 20. Fig. 4 also clearly illustrates the temperature effect in LC–CLENI MS, with a decrease in $[M - R]^-$ and a sharp increase in $[M + Cl]^-$ as the source temperature decreases.

### *LC analysis of pesticides*

The liquid chromatograms of the reconstructed ion current (RIC) traces for a mixture of ten organophosphorus pesticides in the PCI, NCI and CLENI modes are shown in Fig. 5; the presence of chloroacetonitrile did not affect the retention time or peak shape of the analytes. Obviously, NCI is much more sensitive than PCI for this type of compound (*cf.*, refs. 9 and 14). The sensitivity in the NCI mode was 10–20 times better than in the PCI mode for carbophenothion, ronnel, azinphos-methyl and azinphos-ethyl and about four times better for dimethoate, paraoxon-methyl, parathion-methyl, trichlorfon and coumaphos. With vamidothion, the sensitivity in the NCI mode was two times worse than in the PCI mode. This phenom-

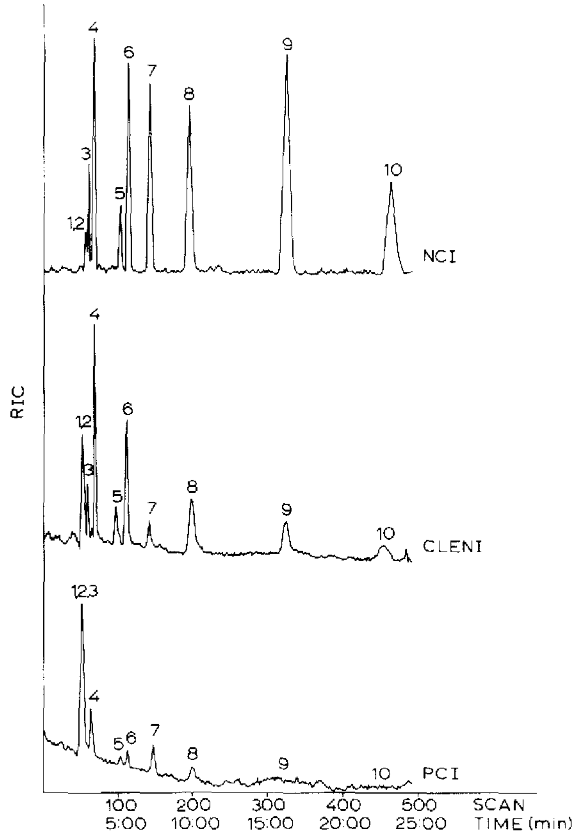

Fig. 5. Reconstructed ion current chromatograms in LC–PCI MS, LC–NCI MS and LC–CLENI MS for a mixture of (1) vamidothion, (2) trichlorfon, (3) dimethoate, (4) paraoxon-methyl, (5) azinphos-methyl, (6) parathion-methyl, (7) azinphos-ethyl, (8) coumaphos, (9) ronnel and (10) carbophenothion. Amount of each component injected, 50 ng; eluent, acetonitrile–water (70:30) for PCI and NCI or acetonitrile–water–chloroacetonitrile (69:30:1) for CLENI at 20 µl/min; scan time, 3 s; ion source temperature, 300°C.

enon has also been observed for other compounds that have an $-NHCH_3$ group such as triazine herbicides, methylurea and carbamate pesticides[9].

Comparing the LC–NCI MS and LC–CLENI MS traces in Fig. 5, it can be seen that for most of the early eluting compounds the sensitivity is similar in both ionization modes. For azinphos-ethyl, coumaphos, ronnel and carbophenothion there is, however, a 4–8-fold loss in sensitivity with CLENI compared with NCI.

In Fig. 5, *ca.* 50 ng of each component were injected on to the LC column. When 5 ng were injected, all LC peaks could still be detected in the RIC trace (NCI mode), but for amounts lower than 1 ng the components could only be detected in the selected ion mode. Detection limits were calculated to be 50 pg (signal-to-noise ratio 3:1), which makes the technique suitable for trace analysis. For comparison, one can quote values reported for GC–MENI MS[14] using selected ion monitoring, which gives a detection limit of about 25 pg for parathion-ethyl.

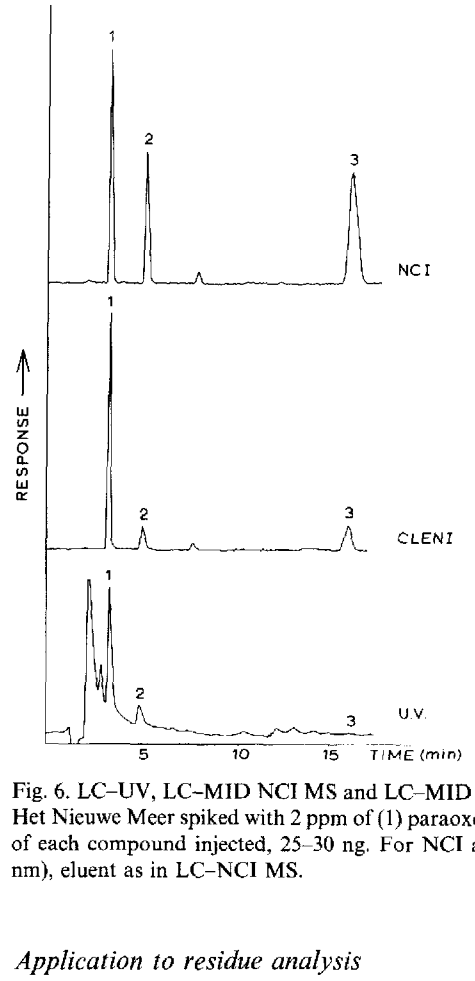

Fig. 6. LC–UV, LC–MID NCI MS and LC–MID CLENI MS traces for a sediment sample from the lake Het Nieuwe Meer spiked with 2 ppm of (1) paraoxon-methyl, (2) azinphos-methyl and (3) ronnel. Amount of each compound injected, 25–30 ng. For NCI and CLENI, conditions as in Fig. 5; for LC–UV (254 nm), eluent as in LC–NCI MS.

### *Application to residue analysis*

Capillary GC–EI MS[13,22,23] or GC–PCI or GC–NCI MS with methane[11–13] or ammonia[23] as reagent gas is frequently the preferred method for the determination of organophosphorus pesticide residues in environmental samples. However, the thermolability and/or high polarity of the compounds easily causes decomposition and/or peak tailing in GC analysis. In addition, the optimization of the column temperature in order to avoid column bleeding is fairly critical in GC–MS. Further, White *et al.*[12] found higher background responses in GC–MS than in moving belt LC–MS; they concluded that the latter technique is more tolerant to co-extractives. Because of this, LC–MS of organophosphorus pesticides is an area of growing interest and it has been applied using a split interface[9,10], a moving belt[12] or thermospray[20] using chemical ionization MS.

In this work, a sediment sample from the lake Het Nieuwe Meer was spiked with 2 ppm of paraoxon-methyl, azinphos-methyl and ronnel. Fig. 6 shows the LC–UV, LC–NCI MS and LC–CLENI MS traces of the sediment after a pre-treatment procedure derived from ref. 17. LC–MS in the multiple-ion detection (MID; 2–5 *m/z* values per analyte) mode is seen to be more selective than LC with UV detection at 254 nm, both with CLENI MS and NCI MS. Further, one should note that ronnel shows no absorption at 254 nm. Its maximum absorption is at 212 nm, which indicates that difficulties may easily arise when screening extracts from environmental samples by LC–UV.

In the LC–NCI MS and LC–CLENI MS traces in Fig. 6 a small peak is observed at a retention time of 7.7 min. With NCI, the mass spectrum of this peak showed fragments at *m/z* 141 (100%), 255 (40%) and 307 (25%) and, with CLENI, two fragments at *m/z* 141 and 307 with 20 and 100% relative intensities, respectively. These fragment ions and the fragmentation behaviour are characteristic of ronnel, *m/z* 141 corresponding to the functional group and *m/z* 307 to $[M - R]^-$. However, the compound can not be ronnel, as this elutes at 16 min (peak no. 3). Probably it is an isomer of ronnel with the same molecular weight and a sulphur–oxygen rearrangement. It is known that the phosphorothionate pesticides containing an aromatic group easily undergo a rearrangement involving an oxygen–sulphur transfer, as shown for parathion-methyl in Fig. 1. This explains its relatively short retention time: the oxygen analogues of phosphorothionates and phosphorodithioates have much shorter retention times[12,22,24] than the original pesticides. Finally, the fragment at *m/z* 255 in LC–NCI MS has not been observed with ronnel and may correspond to the thiophenoxide anion $[M - R_2 - Cl]^-$.

## CONCLUSIONS

The relative merits of LC–PCI MS, LC–NCI MS and LC–CLENI MS have been compared with ten organophosphorus pesticides as test compounds. NCI and PCI generally provide information about the functional group of a pesticide and its molecular weight, respectively. In CLENI an intense $[M - R]^-$ peak is always formed and, in most instances, a relatively intense $[FG]^-$ fragment. For the trace determination of the organophosphorus pesticides, NCI and CLENI are to be preferred to PCI because of their higher sensitivity. Picogram levels can be detected and similar sensitivities to those reported for MENI[14] are obtained. Because the base peak with CLENI is $[M - R]^-$ as against the functional group with NCI, the former mode has the advantage that scanning can be carried out starting from higher *m/z* values, *i.e.*, the chemical noise will be less. Moreover, whereas NCI gives similar mass spectra for many of the studied compounds, CLENI provides more selective information and allows one to distinguish between the different organophosphorus pesticides. DLI LC–MS has successfully been employed in the NCI and CLENI modes to monitor pesticide residues in sediment samples at the low ppm level using a simple pre-treatment procedure. The sensitivity can easily be improved further by using a better injection volume to sample extract ratio (0.5 μl *vs.* 2 ml in the present instance).

The degree of chloride attachment is known to be highly dependent on the ion source temperature. Two aspects should be mentioned. If, in our LC–CLENI MS system, the source temperature was maintained at similar values to those used by Parker *et al.*[10], the relative intensity of the $[M + Cl]^-$ peaks for the various pesticides typically was 15–25 times higher than that in the latter work. As suggested earlier[16], this can be explained by the differences in the LC–MS systems used. Hence, whereas in our experiments a narrow-bore LC system with total introduction of the effluent into the source was used, Parker *et al.* used a conventional LC system with a Hewlett-Packard DLI probe with a variable split (usual ratio 1:99). Secondly, the data obtained so far with our DLI interface suggest (*cf.*, ref. 16) that better results, *i.e.*, higher percentages of chloride attachment, can be obtained if the ion source temperature is kept relatively low, provided, however, that the LC effluent is sufficiently pre-heated in the interface capillary. A new interface has therefore been designed that allows us to regulate the interface and the source temperature independently of each other. Interface optimization will be the focus of our next study, with the two-fold aim of carrying out LC–CLENI MS analyses at lower ion source temperatures and extending the range of analytes to more thermolabile compounds.

## ACKNOWLEDGEMENTS

Dr. D. Barceló is the recipient of a NATO fellowship (Spain). We thank Philips (Eindhoven, The Netherlands) for the loan of a Pye Unicam UV detector.

## REFERENCES

1 T. R. Covey, E. D. Lee, A. P. Bruins and J. D. Henion, *Anal. Chem.*, 58 (1986) 1451A.
2 E. D. Lee and J. D. Henion, *J. Chromatogr. Sci.*, 23 (1985) 253.
3 W. M. A. Niessen, *Chromatographia*, 21 (1986) 277.
4 W. M. A. Niessen, *Chromatographia*, 21 (1986) 342.
5 Y. Ito, T. Takeuchi, D. Ishii and M. Goto, *J. Chromatogr.*, 346 (1985) 161.
6 T. Tsuda, G. Keller and B. J. Stan, *Anal. Chem.*, 57 (1985) 2280.
7 P. Hirter, H. J. Walter and P. Datwyler, *J. Chromatogr.*, 323 (1985) 89.
8 C. E. Parker, C. A. Haney and J. R. Hass, *J. Chromatogr.*, 237 (1982) 233.
9 C. E. Prker, C. A. Haney, D. J. Harvan and J. R. Hass, *J. Chromatögr.*, 242 (1982) 77.
10 C. E. Parker, K. Yamaguchi, D. J. Harvan, R. W. Smith and J. R. Hass, *J. Chromatogr.*, 319 (1985) 273.
11 H. J. Stan and G. Kellner, in W. Baltes, P. B. Czedik-Eysenberg and W. Pfannhauser (Editors), *Recent Developments in Food Analysis, Proceedings of Euro Food Chem. I*, Verlag Chemie, Basle, 1982, pp. 183–189.
12 K. D. White, Z. Min, W. C. Brumley, R. T. Krause and J. A. Sphon, *J. Assoc. Off. Anal. Chem.*, 66 (1983) 1385.
13 A. K. Singh, D. W. Hewetson, K. C. Jordon and M. Ashraf, *J. Chromatogr.*, 369 (1986) 83.
14 K. L. Busch, M. M. Bursey, J. R. Hass and G. W. Sovocool, *Appl. Spectrosc.*, 32 (1978) 388.
15 R. C. Dougherty and J. D. Wander, *Biomed. Mass Spectrom.*, 7 (1980) 401.
16 R. B. Geerdink, F. A. Maris, G. J. de Jong, R. W. Frei and U. A. Th. Brinkman, *J. Chromatogr.*, 394 (1987) 51–64.
17 D. C. G. Muir, N. P. Grift and J. Solomon, *J. Assoc. Off. Anal. Chem.*, 64 (1981) 79.
18 J. A. Apffel, U. A. Th. Brinkman, R. W. Frei and E. A. I. M. Evers, *Anal. Chem.*, 55 (1983) 2280.
19 R. L. Holmstead and J. E. Casida, *J. Assoc. Off. Anal. Chem.*, 57 (1974) 1050.
20 R. D. Voyksner and C. A. Haney, *Anal. Chem.*, 57 (1985) 991.
21 H. P. Tannenbaum, J. D. Roberts and R. C. Dougherty, *Anal. Chem.*, 47 (1975) 49.
22 R. T. Krause, Z. Min and S. H. Shotkeim, *J. Assoc. Off. Anal. Chem.*, 66 (1983) 1353.
23 J. P. G. Wilkins, A. R. C. Mill and D. F. Lee, *Analyst (London)*, 110 (1985) 1045.
24 A. M. Wilson and R. J. Bushway, *J. Chromatogr.*, 214 (1981) 140.