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Determination of chlorinated pesticides by capillary supercritical fluid chromatography–mass spectrometry with positive- and negative-ion detection

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ABSTRACT

An interface between a capillary supercritical fluid chromatograph and a double-focusing mass spectrometer was developed. Modification of the standard electron ionization (EI)–chemical ionization (CI) combination ion source was necessary to obtain useful mass spectra with negative-ion detection. A detection limit in the lower nanogram range of the chlorinated pesticides (DDT and dieldrin) was found irrespective of the mode of detection. Positive-ion methane CI resulted in a relatively abundant $[M + H]^+$ ion, whereas positive-ion isobutane and ammonia CI appeared not to be amenable to the detection of chlorinated pesticides. The EI–charge exchange mass spectra of the investigated pesticides generally did not match the library mass spectra. In the negative-ion mode, CO_2 was an efficient moderating gas giving relatively large amounts of $M^{-\bullet}$, in addition to some fragment ions. More fragmentation was observed when N_2O replaced CO_2 as the mobile phase. No major effects on the mass spectra, obtained by using pure mobile phase, were observed on adding methane, isobutane or ammonia.

INTRODUCTION

Gas chromatography–mass spectrometry (GC–MS) has become an extremely useful technique for the detection and identification of pesticides. Negative-ion chemical ionization (NICI) has great potential because of its selectivity for materials containing electronegative atoms, a property common to most pesticides. Recently, supercritical fluid chromatography–mass spectrometry (SFC–MS) also has been employed for pesticide analysis in both positive- [1,2] and negative-ion [3,4] modes.

Unlike GC, SFC is not restricted by compound volatility or lability, from which some pesticides such as acid and carbamate types suffer. SFC–MS is a relatively new technique. Nevertheless, a wide range of applications has already been demonstrated [5].

One of the main drawbacks of SFC–MS as compared with GC–MS is that library searchable electron ionization (EI) mass spectra are not readily obtained. However, the charge exchange (CE) mass spectra obtained have been reported to resemble the EI mass spectra [2,6]. The

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detection limit in the positive-ion EI mode has been reported to be in the lower nanogram range [3], whereas those in SFC–CI–MS are in the range of tens of picograms in the full-scan mode and comparable to those found in GC–MS analysis [7].

The main aim of this study was to retrofit an interface for capillary SFC to a JEOL double-focusing mass spectrometer. The interface and the necessary instrument modifications are described. Another aim of our study was to investigate the possibility of using the SFC–MS system for pesticide analysis. Hexachlorocyclopentadiene and chlorodiphenylmethane derivatives were used as model substances to investigate the effect of different mobile phases (carbon dioxide and nitrous oxide) and different reagent and moderating gases on the limit of detection (LOD) and mass spectra in both positive- and negative-ion modes.

Even though CO_2 and N_2O have been shown to have nearly identical properties as mobile phases [8], it was of interest to examine their possible difference in behaviour with respect to the mass spectrometric detection of chlorinated pesticides. For negative-ion detection, modifications of the standard ion source were necessary. The influence on the mass spectra using CO_2 as the mobile phase in negative-ion MS was investigated by varying the ion source temperature, amount of mobile phase CO_2 and different CI reagent gases. The results demonstrate that CO_2 acts as a moderating gas.

EXPERIMENTAL

Materials

SFC-grade liquid CO_2 and N_2O were obtained from Scott Speciality Gases (Plumsteadville, PA, USA) and methane, isobutane and ammonia from AGA Norgas (Oslo, Norway). The standards used were obtained from different commercial sources. The compounds were dissolved in HPLC-grade chloroform, dichloromethane or carbon disulphide (Rathburn, Walkerburn, UK).

Columns and restrictors

A 5 m × 50 μm I.D. (375 μm O.D.) SB-phenyl-5 (0.25-μm film thickness) column that

was purchased from Lee Scientific (Salt Lake City, UT, USA) was used throughout. Integral restrictors [9] made of 50 μm I.D. (375 μm O.D.) fused silica (Polymicro Technologies, Phoenix, AZ, USA) and 50 μm I.D. frit restrictors (Lee Scientific) were used. Linear restrictors of 10–25 μm I.D. fused silica (Polymicro Technologies) were used for the dynamic splitting.

Instrumentation

A Model 602 SFC system (Lee Scientific) was used. This instrument is equipped with a C14W injector (Valco) with a 200-nl loop, which can be operated with timed split injection. In addition, a 500 μm I.D. dynamic splitter [10] was installed inside the oven. Injections were performed at or slightly above ambient temperature, while dynamic splitting occurred under supercritical conditions. The column was installed in the dynamic splitter at a position 2–3 mm below the injector rotor. The split restrictor was heated by an extra heating unit (copper block) with temperature control (Eurotherm, Worthing., UK). The heating unit was located outside the oven.

The column and the restrictor were connected by a 400 μm I.D. butt connector (Lee Scientific) between the oven and the MS instrument. An oven temperature of 100°C was used and, if not mentioned otherwise, a linear pressure programme from 100 to 250 bar.

A 3-kV JMS-DX 303 double-focusing mass spectrometer (JEOL), of EB geometry, equipped with a 10-kV post-acceleration conversion dynode detector was used for detection. An electron ionization–chemical ionization (EI–CI), an LC ion source and a modified version of the LC ion source were used. The LC ion source was also a dual EI–CI ion source (Fig. 1).

A thoriated iridium filament (Interion, Manchester, UK) replaced the original rhenium filament. This filament cannot be easily welded, therefore the filament holder was modified to allow for attachment by two screws (all new parts were made of stainless steel 316). The filament current limit had to be increased compared with that used for rhenium filaments in order to obtain a satisfactory emission from the thoriated iridium filament.
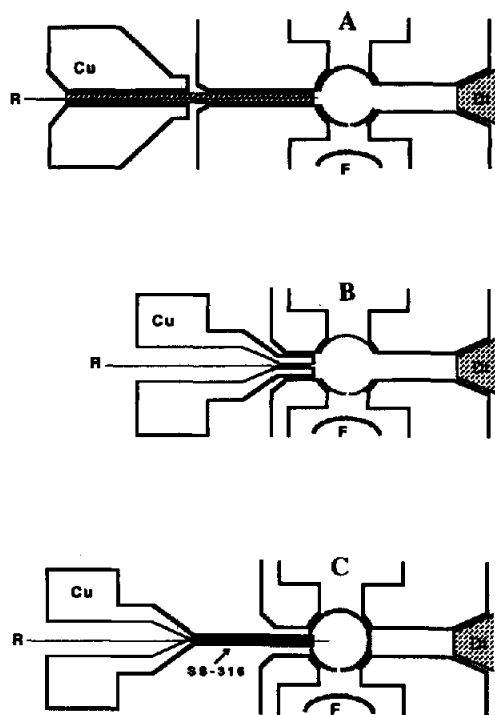
Fig. 1. (A) EI–CI ion source with restrictor heating unit (not to scale). The heating zone is 4 cm × 0.8 mm I.D. (stainless steel). (B) LC ion source with restrictor heating unit (not to scale). The heating zone is 5 mm × 0.5 mm I.D. (copper). (C) Modified LC ion source with restrictor heating unit (not to scale). The heating zone is 2 cm × 0.5 mm I.D. (stainless steel). The EI–CI and LC ion sources can be operated in the EI mode (without the inner circle) and in the CI mode, whereas the modified ion source can be operated in the CI mode only. R = Restrictor (the approximate restrictor outlet position is indicated in the drawings); Cu = copper heating block; DI = direct insertion probe (closing the outlet); F = thoriated iridium filament; SS-316 = stainless steel.

The restrictor was connected to the mass spectrometer through the GC–MS entrance of the ion source housing through a 1/4 in. O.D. glass tube (1 in. = 2.54 cm). The restrictor changing procedure requires that the ion-source housing is exposed to atmospheric pressure. However, the complete procedure usually requires less than 20 min, including heating to the operating conditions. Different restrictor heating designs (Fig. 1) were investigated, depending on the choice of ion source. In all instances the LC interface controller of the MS supplied the electric current for the heaters and temperature monitoring. The approximate restrictor positions

used are indicated in Fig. 1. Fine adjustment of the restrictor position was performed depending on the flow-rates and operating temperatures. A restrictor heater temperature of 300°C was used if not mentioned otherwise. The transfer line between the SFC and MS systems can be heated to constant temperature, using the heating unit of the GC–MS interface. However, heating of the transfer line was not necessary for the compounds investigated in this study.

In order to use high CO_2 flow-rates, the apparent CO_2 pressure could be reduced by introducing liquid nitrogen into the liquid nitrogen trap of the mass spectrometer. For a linear flow-rate of about 1.7 cm/s of supercritical CO_2 at 100 bar, a pressure of about $2 \cdot 10^{-5}$ Torr (1 Torr = 133.322 Pa) was measured in the ion source housing. When liquid nitrogen was introduced into the trap, less than $2 \cdot 10^{-6}$ Torr was measured. Cryotrapping of CO_2 and N_2O allowed the use of flow-rates higher than 3 cm/s also in the CI mode. No noticeable difference in LODs and mass spectra were observed with or without cryotrapping.

The mass spectrometer was operated with electron multiplier voltages of about 1.5 kV and an ionization current of 100 μA throughout. EI–CE mass spectra were obtained using an electron energy of 70 or 22 eV and CI mass spectra were obtained using 230 eV in both the positive- and negative-ion modes. All data were recorded with a mass resolution of 500.

RESULTS AND DISCUSSION

Filament

A substantial background signal in the mass range m/z 180–270 was observed on introduction of CO_2 into the ion source in the EI–CE mode when using a rhenium filament. The background level increased slightly with increasing mobile phase flow-rate and was strongly enhanced when solutes entered the ion source. The effect was most pronounced for oxygen-containing compounds such as alcohols and carboxylic acids, less for polyaromatic hydrocarbons and alkanes. The background signal was caused by thermochemical reactions with the hot rhenium filament, as was evident by the presence of several

rhenium oxide species [11] in the background mass spectra. A similar effect was observed with a tungsten filament. Installation of a thermospray-type thoriated iridium filament eliminated this problem. This filament was also used with N_2O as mobile phase without any background problem. The thoriated iridium filament has therefore been used throughout this study, and as the filament lifetime was observed to be >400 h, we can recommend this type of filament.

Positive-ion MS

EI–charge exchange. It has been argued that when CO_2 is used as a mobile phase and the ionization potential of the sample molecule is lower than the recombination energy of CO_2^+ (13.8 eV), CE ionization is achieved [12]. However, it has also been pointed out that ionization by the CE mechanism requires the use of a higher ion source pressure (0.5–1 Torr) and a higher electron energy (200–500 eV) [3]. It is not possible to measure the actual pressure in the ion source of this mass spectrometer. The ion sources are relatively open in the EI mode, and this implies that the pressure in the ion source may be close to the measured pressure in the ion source housing in this mode (without cryotrapping), whereas the pressure in a more closed CI ion source is much higher. The maximum ionization energy was 70 eV in the EI mode. However, it was observed that a reduced electron energy resulted in improved signal-to-noise ratio, mainly owing to a reduced background signal level in the low-mass range (m/z 50–100). The larger amount of background fragment ions using 70-eV electrons may be caused by the exothermicity of EI and not the CE mechanism. As it is difficult to establish whether the ionization of our sample molecules is due to EI, CE or a dual EI–CE mechanism, we have used the notation EI–CE ionization when the instrument was operated in the EI mode.

Detection limits, calculated as amount injected on to the column giving a signal-to-noise ratio of 3 in the full-scan mode, were investigated for different types of compounds in addition to the chlorinated pesticides. A detection limit in the lower nanogram range was found for polycyclic

aromatic hydrocarbons, fatty acid ethyl esters and polystyrenes. The detection limits for different chlorinated pesticides were in the range 2–4 ng. As large variations in injector loop size have been reported [13], and the dynamic splitting ratio may be difficult to control, only approximate values are reported. These detection limits are in the same range as reported in the literature [3].

In the mass spectrum of DDT the main process observed is loss of HCl and CCl_3 and molecular ion $M^{+\bullet}$ has a low abundance. This is different from the results of Houben et al. [2] and the library mass spectrum of DDT, where $M - CCl_3^+$ yields the base peak. However, the main fragment ion observed of DDD was $M - CHCl_2$, and a relatively smaller amount of $M - CHCl$. The mass spectrum of dieldrin was complex, and compared with the EI library mass spectrum less fragmentation was observed. However, the mass spectrum of aldrin resembled the EI library mass spectrum. Therefore, as EI-like mass spectra were not obtained in all of our experiments, the identification of chlorinated pesticides using library mass spectra is not feasible.

CI with methane as reagent gas. The LODs for dieldrin and DDT are in the range 1–4 ng using
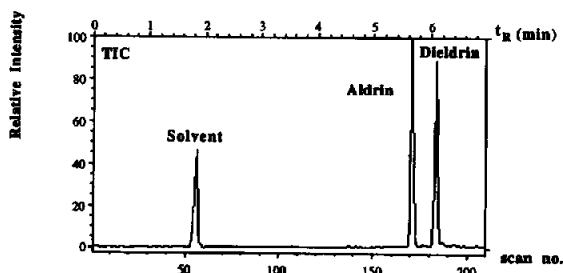

Fig. 2. Total ion current chromatogram of aldrin and dieldrin obtained with positive-ion methane CI using the modified LC ion source. A 0.5 mg/ml (in CS_2) solution and a 1:12 splitting ratio result in about 8 ng of each compound being injected on to the column. SFC conditions: column temperature 100°C and pressure programming: 100 bar (2 min), then increased from 100 to 250 bar at 20 bar/min (linear gradient). MS conditions: restrictor heating temperature 300°C, ion-source temperature 135°C and scanning from m/z 100 to 600 at 2.0 s per scan. The solvent peak is due to clusters of CS_2.

both CO_2 and N_2O as mobile phases. In the chromatogram shown in Fig. 2 about 8 ng of each compound were injected. A slightly lower LOD and a relatively larger amount of $[M + H]^+$ were obtained using the modified ion source (Fig. 1C) than with the standard EI–CI ion source. The mass spectra of these compounds are shown in Fig. 3A and B.

Compared with the reported methane CI mass spectra of dieldrin and aldrin [14], a relatively

larger amount of $[M + H]^+$ was found in this work. This may be explained by better conditions for ion–neutral reactions and hence an increase in stabilized ions.

CI with isobutane as reagent gas. When isobutane replaced methane as the reagent gas a less favourable LOD (6–10 ng) was obtained for the chlorinated pesticides using CO_2 as mobile phase. The detection limit was >30 ng using N_2O as mobile phase, so no further experiments
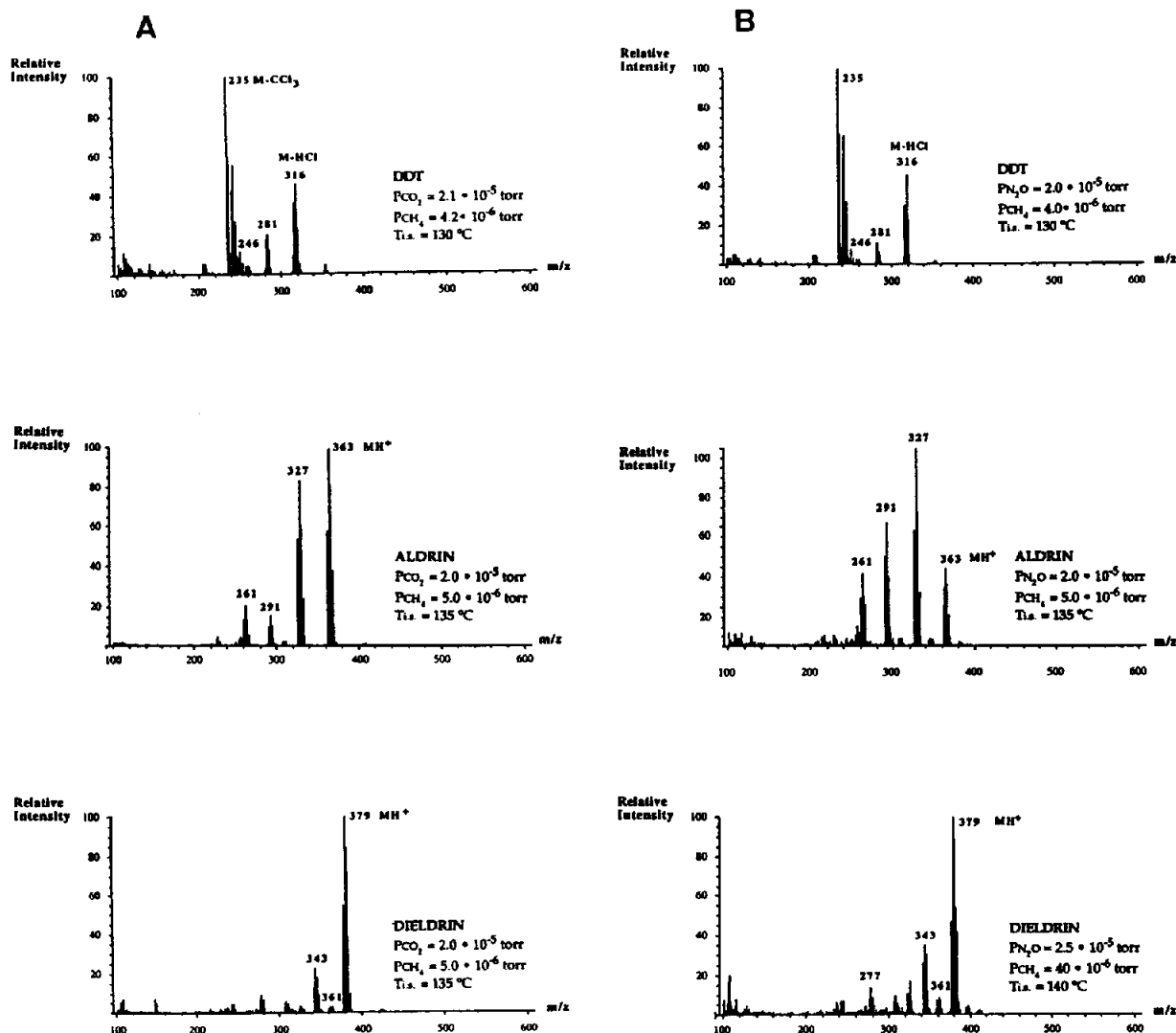

Fig. 3. Positive-ion methane CI mass spectra of dieldrin, aldrin and DDT using (A) supercritical CO_2 and (B) supercritical N_2O as mobile phase. The EI-CI ion source (Fig. 1A) was used. Ion-source pressure is given as $P_{CO_2} + P_{CH_4}$ and ion-source temperature as $T_{i.s.}$.

were carried out with this combination of mobile phase and reagent gas.

However, the LOD for anthracene and chlorinated anthracene was in the lower nanogram range using both CO_2 and N_2O as mobile phase, and $[M + H]^+$ were the main ions. Isobutane alone has been reported to give useful mass spectra of chlorinated pesticides in both positive- and negative-ion modes [15]. The major ions in each of the reported mass spectra may be accounted for by dissociative proton transfer and hydride and chloride abstraction involving $C_4H_9^+$. Our results indicate that the proton affinity of the investigated compounds is less than that of isobutane as protonated molecular ions are absent.

CI with ammonia as reagent gas. Ammonia has been used as the reagent gas [5,16–21] for a great variety of compounds in positive-ion CI. When CO_2 and ammonia were used as mobile phase and reagent gas, respectively, the chlorinated pesticides could be detected as peaks (LOD *ca.* 2–4 ng) in the chromatogram, but the mass spectra did not give any structural information. The mass spectra were dominated by the fragment ion at m/z 130 that was present at a constant level throughout the chromatogram, but increased when compounds and the solvent CS_2 were eluted. Similar effects have been observed by others [22] using ammonia as reagent gas. No $[M + H]^+$, $[M + NH_4]^+$ or any sample-containing ions were observed for compounds with large electron-capture cross-sections. The m/z 130 ion found in our work may originate from a $[(CO_2)(NH_3)_5H]^+$ cluster. The ammonia pressure used was about $4.0 \cdot 10^{-6}$ Torr. From the negative-ion MS experiments we know that the CO_3^- ions are present in the ion source, and may neutralize m/z 130 ions. Hence, if compounds introduced into the ion source are ionized by the CO_3^- ions, fewer of the CO_3^- ions will be available for the m/z 130 neutralization. Hence an increase in the m/z 130 level may be observed.

Negative-ion MS

Electron-capture and ion–neutral reactions are the two main ionization techniques that are used in this mode [23]. The soft nature of these processes is an advantage when molecular ions are wanted. For the electron-capture process, the choice of moderating gas, among other parameters, is considered as an important factor for the yield of $M^{-\bullet}$.

The results obtained in the negative-ion mode using the original EI–CI ion source was very discouraging; both high LODs and extensive fragmentation were observed. However, successful SFC–negative-ion MS has been reported by others also on chlorinated pesticides [3,4].

The reason for the high ratio of fragmentation in our experiments is the low pressure in the ion source, which implies a smaller amount of thermalized electrons. We therefore modified the ion source (LC version) to obtain a higher pressure in the ion source. This modified ion source was used throughout our experiments in negative-ion MS.

It soon became apparent that an ion-source temperature lower than 220–300°C (which is normally used in SFC–positive-ion CI–MS [7]) improved the mass spectra. Temperatures above 200°C , as used by Huang *et al.* [4], led to extensive fragmentation and a high LOD of dieldrin. Thus, in most of the reported experiments, a temperature of about 150°C was used. Even better results with respect to LOD and reduced fragmentation were obtained in our experiments when the temperature was lowered to about 70°C. However, this temperature could not be used over a long period of time, owing to the heat supported by the filament and restrictor heater. The possibility of cooling the ion source thus appears to be a necessary requirement. An ion-source temperature of about 140°C was used by Roach *et al.* [24], who also pointed out the necessity of using lower temperatures in negative-ion MS.

A repeller potential of 0 V was used throughout all the negative-ion mode experiments, as this potential will increase the residence time of molecular ions and electrons, and hence increase the collision probability with the moderating gas molecules (third-body collisions). Such conditions are necessary to obtain collisional stabilization of excited ions.

CO_2 as moderating gas. CO_2 is considered to be a slightly more efficient moderating gas than

isobutane, which in turn is more efficient than methane [23]. The use of CO_2 as moderating gas has also been reported to give relatively simple mass spectra, usually without unexpected ions [23]. The observation of a fragment ion of m/z 60 throughout our experiments may be explained by fragmentation of CO_2 clusters [25].

When CO_2 is used as the mobile phase it may also act as a moderating gas. Fig. 4 shows the mass spectra obtained for endrin using CO_2 as mobile phase and moderating gas. An apparent
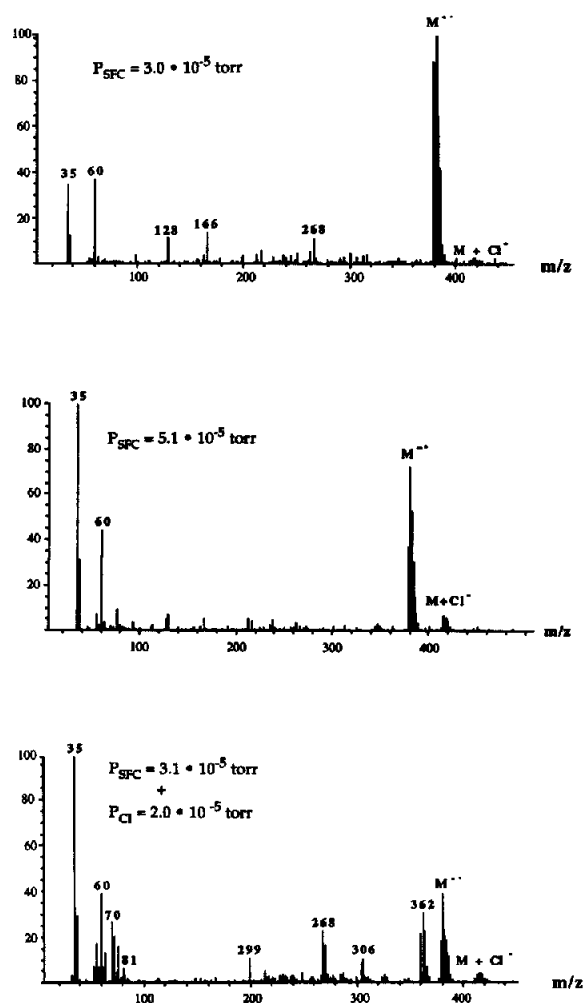

Fig. 4. Negative-ion mass spectra of endrin using CO_2 as a moderating gas. The ion source pressure caused by the mobile phase CO_2 is denoted by P_{SFC}. P_{CI} refers to the pressure of the CO_2 gas introduced through the CI reagent gas transfer line. The ion source temperature was 70°C and the modified LC ion source was used.

difference in mass spectra is observed. When mobile phase CO_2 is the only source of CO_2, very little fragmentation occurs and $M^{-\bullet}$ dominates the mass spectrum. This is thought to be caused by a more efficient production of thermalized electrons. Adiabatic cooling cause a moderating gas with a lower thermal energy compared with the buffer gas introduced via the CI inlet system. The lower thermal energy of mobile phase CO_2 gas molecules results in a higher efficiency of primary electron quenching and hence in an increased loss of energy of the latter [26]. Secondary electrons are thermalized electrons which may have an energy of about 0.1 eV, which is wanted for resonance electron capture. The reduced thermal energy of the buffer gas is caused by the formation of neutral clusters, as a consequence of adiabatic expansion. The cluster production will give a relatively high local density in the thermalization area and hence a higher thermalization efficiency of the electrons. The consequence of the factors mentioned above is a decreasing exothermicity of the ionization process, which in turn implies an increased amount of molecular ions. The use of an electron energy lower than 230 eV of the primary electrons did give a slight improvement with respect to detection limits.

The negative-ion mass spectrum of dieldrin, using CO_2 as moderating gas, is shown in Fig. 5A. The $M^{-\bullet}$ ion is also present for this compound, but other fragment ions dominate the mass spectrum. This mass spectrum was obtained using a higher temperature than that used for endrin. The limit of detection for the investigated pesticides was about 2–4 ng. If the measured pressure became higher than $2.5 \cdot 10^{-5}$ Torr, quenching of the signal and thus higher LODs were observed

N_2O as moderating/reagent gas. The mass spectrum obtained for dieldrin using N_2O as mobile phase with no additional reagent gas is shown in Fig. 5B. A smaller amount of $M^{-\bullet}$ is found than when CO_2 was used as the mobile phase (Fig. 5A). The main differences in the mass spectra utilizing CO_2 and N_2O as mobile phase are due to the ionization process. When N_2O is used, the main ionization process is caused by CI, which is a more energetic reaction
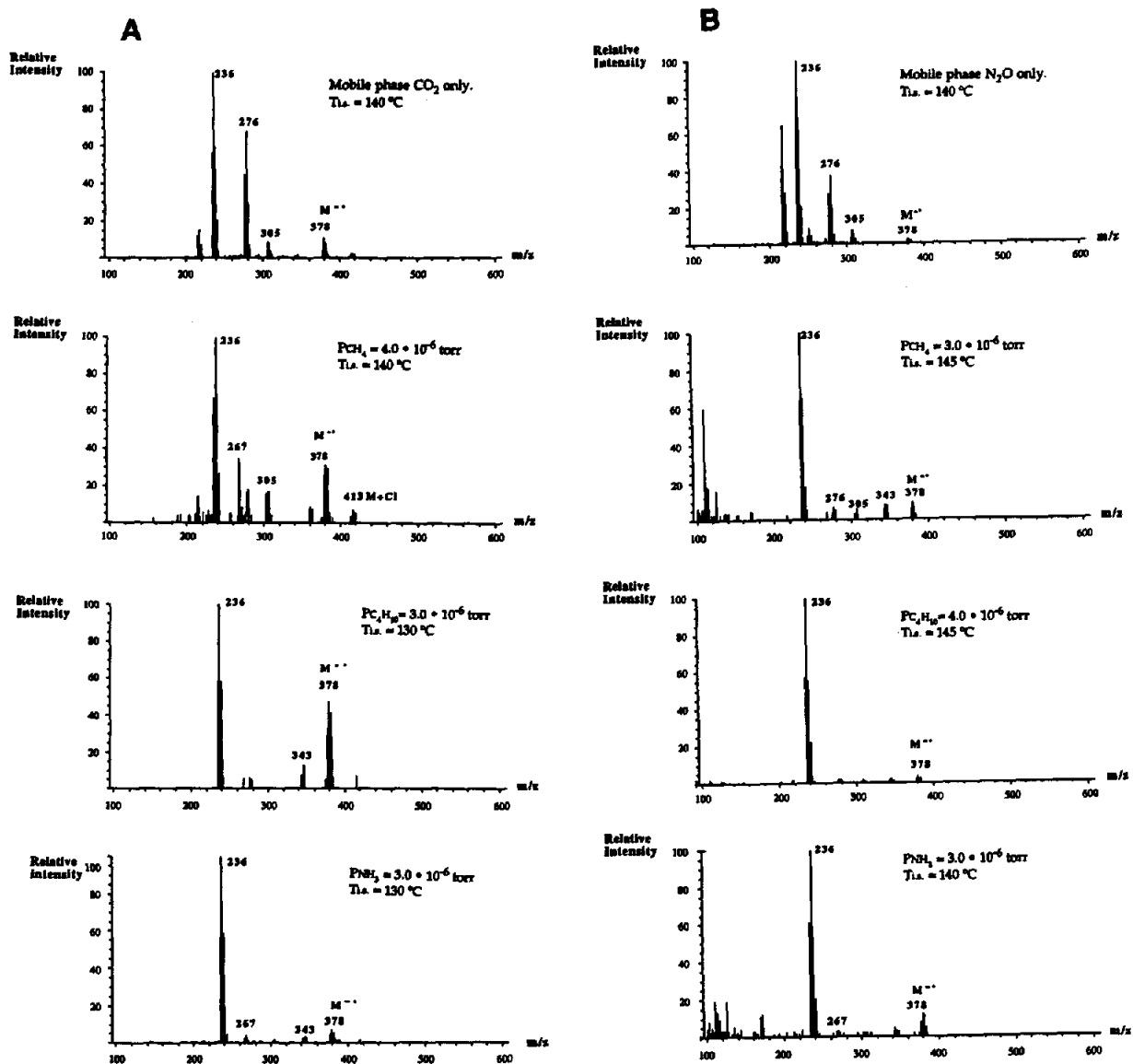
Fig. 5. Negative-ion mass spectra of dieldrin using (A) supercritical CO_2 and (B) supercritical N_2O as mobile phases. Ion-source temperatures and pressure of the added gases are given. The modified LC ion source was used. The ion-source pressure due to mobile phase only was about $2 \cdot 10^{-5}$ Torr when dieldrin was eluted using a pressure programme from 100 to 250 bar.

than electron attachment by thermalized electrons.

The main conclusion to be drawn from these experiments is that CO_2 is preferred when electron attachment is wanted and N_2O when reagent ions [23] are required for CI. The LODs were in the range 2–4 ng.

Methane as moderating/reagent gas. Methane is also classified as a moderating gas in negative-ion MS [23]. However, in combination with N_2O, the reagent ion OH^- will be present. The mass spectra of dieldrin shown in Fig. 5 indicate that the combination of CO_2 or N_2O with methane results in ionization caused by an elec-

tron-capture mechanism also. Compared with the negative-ion methane mass spectrum of dieldrin [27], several differences are observed. The reported $[M + Cl]^-$ and $[M + O - Cl]^-$ ions cannot be observed in Fig. 5B. However, the abundant fragment ion at m/z 236 which is the dominant fragment in Fig. 5B was not revealed in the reported mass spectrum. The ion of m/z 236 may be due to $C_5Cl_5^-$. The LODs were in the range 2–4 ng.

Isobutane as moderating/reagent gas. Isobutane itself is reported to be a better moderating gas than methane, and may give reagent ions in mixtures with N_2O [23]. The mass spectra of dieldrin obtained with isobutane as reagent gas are also shown in Fig. 5. The m/z 236 fragment is the dominant fragment using both CO_2 and N_2O as mobile phase.

Relatively more of $M^{-\bullet}$ is preserved when using CO_2 as mobile phase, as is the case using mobile phase alone. These results indicate that both the mobile phases and the added gas function as moderating gases in these experiments. The LODs were in the range 2–4 ng.

Ammonia as reagent/moderating gas. The mass spectra of dieldrin obtained using ammonia as an additional reagent gas (Fig. 5) resembled those obtained using the other gases, with only minor differences in the relative intensities of the fragment ions. Thus, in our experiments, ammonia seems to function as a moderating gas only. It has been reported [4] that pesticides and herbicides gave essentially the same mass spectra using neat CO_2, $CO_2 + CH_4$ and $CO_2 + NH_3$. However, both $M^{-\bullet}$ and MH^- were observed in polyisocyanate mass spectra using CO_2 and ammonia [28]. The LODs in our study were in the range 2–4 ng.

CONCLUSIONS

The interfacing of capillary SFC with a JEOL double-focusing mass spectrometer equipped with GC and LC interfaces was fairly simple. A thoriated iridium filament had to be used instead of a rhenium filament, which gave a severe background of rhenium oxides.

The detection limits obtained, measured as nanograms of sample injected on-column and

with full-scan detection, were in the lower nanogram range, irrespective of the mode of detection, *i.e.*, positive-ion EI–CE, positive-ion CI or negative-ion detection. This is not in accordance with other reports on detection limits. Our results using negative-ion detection are inferior to those observed by others [4] using double-focusing MS. The discrepancies in reported LODs may be caused by the different instrumental designs. Modification of the standard ion source was necessary to obtain useful mass spectra in the negative-ion mode, and further modifications are necessary to improve the LOD.

The EI–CE mass spectra of the investigated chlorinated pesticides did not all match the EI library mass spectra, thus making identification without the use of standards difficult. A relatively abundant $[M + H]^+$ ions was found in the positive-ion methane CI mass spectra, whereas isobutane and ammonia CI were not suitable for the detection of chlorinated pesticides.

In the negative-ion mode, CO_2 was shown to be an efficient moderating gas, giving relatively large amounts of $M^{-\bullet}$. The mobile phase CO_2 cooled by adiabatic expansion was more effective than CO_2 added through the CI reagent gas transfer line in producing thermalized electrons.

Apparently, the mobile phase N_2O also functions as a moderating gas, as the same fragment ions were observed as with CO_2. However, the differences in intensity are pronounced. Addition of methane, isobutane or ammonia did not dramatically change the mass spectra obtained using CO_2 or N_2O alone as mobile phase. Hence electron capture seem to be the dominant mechanism with all the investigated combinations of gases. The possibility of obtaining both $M^{-\bullet}$ and fragment ions is most useful for the identification of chlorinated pesticides.

This work demonstrates that capillary SFC–MS may be a valuable tool in analyses for chlorinated pesticides, offering the possibility of both positive- and negative-ion modes of detection. The detection limits in the low nanogram range may not be a restriction compared with GC–MS analysis, as other injection techniques in which larger volumes may be introduced can be used [29].

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