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GAS CHROMATOGRAPHIC DETECTION OF SELECTED ORGANOCHLORINE SPECIES USING AN ALTERNATING CURRENT PLASMA DETECTOR

ROBERT B. COSTANZO and EUGENE F. BARRY*
Department of Chemistry, University of Lowell, 1 University Avenue, Lowell, MA 01854 (U.S.A.)
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SUMMARY

The alternating current plasma detector for gas chromatography is shown to be a useful detector for selective organochlorine detection. The detector incorporates a simple design and a power source that produces a stable discharge which does not extinguish under high solvent concentration conditions. The plasma discharge produces diatomic emission of CCl species, with few atomic chlorine emission lines. Detection limits for various organochlorine compounds are approximately 1.0 ng/s. The detector exhibits a complex response dependent on molecular structure and environment. Detector selectivity towards CCl *versus* C_2 emission is presented, along with various selective chlorine detection applications in complex matrices.

INTRODUCTION

Many different kinds of organochlorine compounds are introduced into the environment each year through human activities. Analysis of many chlorinated organics is commonly done by packed or high-resolution capillary column gas chromatography (GC) equipped with a halogen-selective detector[1], the most common of which are the Hall electrolytic conductivity detector (HECD) and the electron-capture detector (ECD)[2–5]. Both detectors provide pg/s detection limits and high selectivity for halogens. However, these detectors are prone to contamination by interfering impurities in the chromatographic system or sample, such as water, by detector overload of halogenated compounds and by septum and column bleed[6,7].

Microwave-induced plasma (MIP) detection incorporating the Beenakker cavity TM_{010}[8] is finding continued success due to its ability to selectively distinguish between types of halogens, limits of detection in the pg/s range and ability to do multi-element determination[9–12]. The MIP also has a uniform relative response to most organochlorines per unit mass. Therefore, molecular structure does not influence the detector response, allowing empirical formula determination[13,14].

The direct current plasma detector (DCPD) for GC, sustained in a helium or argon atmosphere, is also a sensitive and selective detector in many applications[15–17]. Both two- and three-electrode configurations are used for selective detection of metallic and non-metallic elements at detection limits between the nanogram to

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picogram range. The incorporation of GC–inductively-coupled plasma (ICP) as an element selective detector continues to show little use compared to GC–MIP; although, detection limits for the metallic and non-metallic elements vary from the microgram to nanogram range and selectivity ratios are high[18,19]. Improvements in the GC interface problems encountered in this technique may help to widen the range of applications and performance enjoyed currently. The helium afterglow detector for GC shows great potential as an element selective detector, since detection limits and selectivities rival values found for GC–MIP[20,21].

Recently, our laboratory developed an alternating current plasma detector (ACPD) for selective capillary GC detection[22,23]. The ACPD is similar to a d.c. microarc plasma source[24] and can tolerate high mass flow-rates of solvent without extinguishing and, therefore, requires no venting valve. This leads to a less complex interface design and minimizes band broadening. The plasma is self-seeding and reignites itself every half cycle, which is 120 times per second for a 60-Hz power supply. As a result, a tesla coil is not required to initiate the plasma as long as the a.c. voltage supply is above the breakdown voltage. This communication describes the detection of a number of chlorinated species, polychlorinated biphenyls (PCBs) and pesticides by capillary GC–ACPD. Linearity, detection limits, selectivity and applications are discussed.

EXPERIMENTAL

Materials

The organochlorine compound standard solutions were prepared in spectra-grade *n*-pentane (Fisher Scientific, Fair Lawn, New Jersey, U.S.A.). The organochlorines used in the study were as follows: tetrachloroethylene, *n*-dodecane, *n*-nonane, *o*-chlorotoluene (Aldrich, Milwaukee, WI, U.S.A.); *p*-dichlorobenzene, 1,5-dichloropentane, Aroclor 1254 (Chem Service, West Chester, PA, U.S.A.); 1,10-dichlorodecane, carbon tetrachloride (Eastman Kodak, Rochester, NJ, U.S.A.); 1,2-dichloroethane (Fisher Scientific, Fair Lawn, NJ, U.S.A.); lindane (Polyscience Corp., Niles, IL, U.S.A.); number 2 fuel oil; regular gasoline (Texaco, White Plains, NY, U.S.A.). The carrier and make-up helium gas were filtered with moisture, oxygen and hydrocarbon traps (Supelco, Bellefonte, PA, U.S.A.).

Instrumentation

The GC–ACPD system arrangement, described in detail elsewhere[22], is shown in Fig. 1 and includes a Hewlett-Packard model 5890A gas chromatograph (Hewlett-Packard, Palo Alto, CA, U.S.A.), a single-beam McPherson grating monochromator EU700 (McPherson, Acton, MA, U.S.A.), an optical bench equipped with an adjustable optical mount and 75-mm biconvex quartz lens (Oreil, Stratford, CT, U.S.A.), a R212 PMT (Hamamatsu, Middlesex, NJ, U.S.A.) coupled to a McPherson Model 7640 voltage supply and a Hewlett-Packard 3392A integrator. The two fused-silica capillary megabore columns employed in this study were a 30 m × 530 μm I.D. column with a 1.5-μm film thickness of DB-1 (J & W Scientific, Cordova, CA, U.S.A.) and a 10 m × 530 μm I.D. column with a 4.8-μm film thickness of CP SIL-8 CB (Chrompack, Bridgewater, NJ, U.S.A.). Table I lists general operating conditions for the GC and ACPD employed throughout the studies. The GC–ACPD interface has

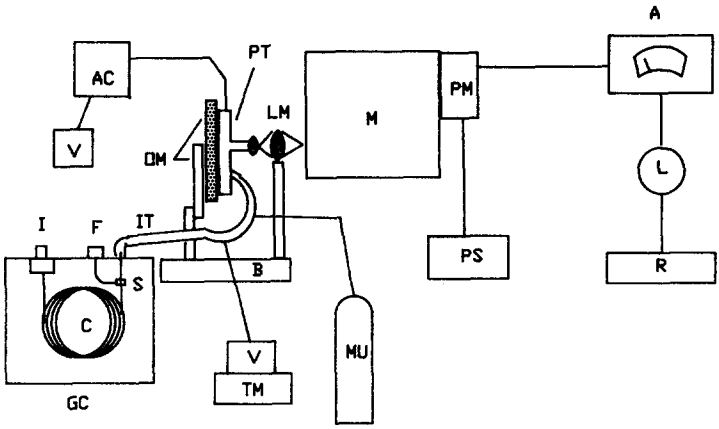

Fig. 1. Schematic diagram of the GC–ACPD experimental arrangement. (GC) gas chromatograph; (C) megabore capillary column; (I) injection port; (F) FID; (S) column oven tee split; (IT) detector interface tube; (V) variac; (AC) a.c. power supply; (OM) optical plasma mount; (PT) plasma discharge tube; (LM) lens and mount; (MU) helium make-up gas; (B) optical bench; (TM) thermocouple thermometer; (M) monochromator; (PM) photomultiplier tube; (PS) PMT power supply; (A) picoammeter; (L) low-pass filter; (R) recorder integrator.

also been described in detail by the authors[23] and includes a PTFE union adaptor that created an electrical barrier between the flexible metal interface capillary column jacket and the 1/8 in. O.D. × 8 in. copper electrode tube. The megabore column is inserted through the interface tube/electrode and a series of rubber septa for electrical insulation. The column is inserted through the middle of the bottom electrode so that 1 mm of the column extends beyond the tip of the electrode. The interface unit is then attached to a Pyrex discharge tube with a 1/4 in. O.D.[23] and mounted onto the optical bench.

Procedure

The optimal operating parameters for the ACPD were previously determined[23] and were employed in the present study, listed in Table I. The optimal helium make-up gas flow-rate was established at 1 ml/min for this study. The low make-up flow-rate

TABLE I

GENERAL GC–ACPD OPERATING CONDITIONS USED IN THE STUDY

Parameter	*Condition*
Injector temperature	230°C
Interface temperature	210°C
Column flow-rate	20 ml/min
Helium make-up flow rate	1 ml/min
a.c. power output	11 000 V a.c.
PMT voltage	1000 V d.c.
Slit width	1500 μm
Low-pass filter time constant	0.11 s
Analytical emission band for the C–Cl species	278.84 nm

results from the fact that since the column flow-rate is rapid (20 ml/min), a 1 ml/min flow serves only to minimize turbulance and create an outside flow pattern. As a result, this flow pattern serves as a sheath and directs the sample vapor plugs into the center of the plasma plume and minimizes the solute skirting the plume. The window arm of the discharge tube was directed to the monochromator and the plasma emission was focused for a maximum signal at a copper wavelength by adjusting the optical mount. The chlorine lines and C–Cl diatomic species bands were obtained by purging a helium stream saturated with chloroform vapor through the plasma and scanning the appropriate wavelength regions. The region scanned was 270.0–800.0 nm at 0.5 nm/s. A smaller region was examined more closely between 230 nm and 330 nm and yielded a few intense diatomic C–Cl analytical emission bands as well as C_2 emission bands. The diatomic species, C–Cl, produced the most intense emission band, which was employed as the analytical emission band in the study.

Standard solutions of 1,10-dichlorodecane (DCD), *p*-dichlorobenzene (DCB), tetrachloroethylene (TCE) and *n*-butylchloride (NBC) were chromatographed at oven temperatures of 150, 80, 50 and 85°C, respectively, on the DB-1 megabore column. The appropriate injection volumes and split ratios were established for each compound in order to introduce the desired amounts into the ACPD. Calibration curves were then constructed from the response data and the detection limits were determined. The selectivity was established by examining a response mixture containing 164 ng C–Cl as DCD and 541 ng C_2 as dodecane in a 0.5-μl injection on the DB-1 megabore column at a split ratio of 16.5 to 1. The separation was achieved at a column temperature of 40°C (0.5 min) to 185°C (10 min) at 7 °C/min, 20.5 ml/min, slit width of 1000 μm with a 1-mm slit height and the output voltage of the detector is governed by a picoammeter setting of 0.3 mA full scale.

The relative response study was performed by recording the response of the ACPD per unit mass of C–Cl for select organochlorine substances that included saturated and unsaturated moieties and contained only one C–Cl per molecule. The GC column used was the CP SIL-8 CB megabore capillary column at a temperature of 32°C (0.5 min) to 150°C at 10°C/min. Applications were done at GC conditions listed in the corresponding figure captions. First, a mixture of volatile organochlorine compounds, each in the amount of 1000 ng, was made in 1 ml of *n*-pentane. A 10-μl injection of the head vapor was introduced onto the CP SIL-8 CB megabore capillary column, described previously. Next, a gasoline sample was spiked with a known amount of lindane and a known aliquot was injected with subsequent detection by FID and ACPD. The detection of Aroclor1254 in diesel gas was done by spiking a 10-ml aliquot of number 2 fuel oil with 10 mg of Aroclor 1254 and injecting 1 μl onto the CP SIL-8 CB megabore column.

RESULTS AND DISCUSSION

Analytical emission bands

The emission profile associated with the plasma emission within the range of 230 nm to 300 nm is depicted in Fig. 2. There are numerous molecular emission bands associated with C_2, CN, CH and C–Cl diatomic emission between 250 nm and 280 nm. Between the two C–Cl bands displayed in Fig. 2 centered at 277.83 nm and 278.84 nm (peaks a and b in Fig. 2), respectively, there is an intense C_2 band (c) which also

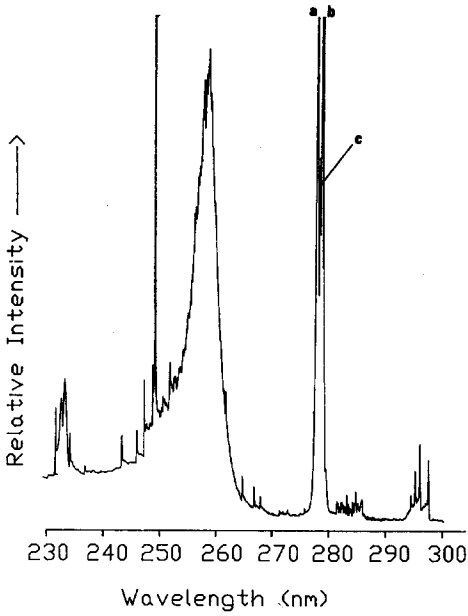

Fig. 2. Wavelength scan of helium saturated with chloroform vapor by the ACPD. Scan rate was 0.5 nm/s with a chart speed of 1 cm/min. (a) CCl 277.83 nm; (b) CCl 278.84 nm; (c) C_2 interference emission band *ca.* 277.0 nm to 278.9 nm.

overlaps with peaks a and b. Peak a is less intense than band b; therefore, the analytical C–Cl emission band used in the entire study was the 278.84 nm band for selective chlorine detection. Dagnall *et al.*[25] and McCormack *et al.*[26] also employed this C–Cl emission band for selective chlorine determination for GC–MIP applications. Most chlorine detection by GC–MIP utilizes the 479.5 nm lines characteristic of atomic chlorine emission, which is an atomic chlorine line. However, helium-MIP is typically a more intense emission source than a.c.-arc techniques, which leads to predominately atomic emission lines. The emission spectra of chloroform generated in this study, which was from 210 nm to 800 nm, showed no chlorine atomic emission that was sufficiently intense for analytical use and showed only a few intense diatomic C–Cl emission bands existed for potential use. However, many of these C–Cl bands are overlapped by very intense C_2 bands, rendering them useless.

A slit width of 50 μm (bandpass of 0.09 nm) yielded sufficient resolution to determine atomic and molecular emission. However, intense molecular emission throughout the spectral region may have masked potential atomic chlorine emission, particularly in the region between 320 nm and 450 nm where many atomic chlorine lines lie[27]. The percentage of C_2 at 278.63 nm (peak c in Fig. 2) which overlaps with the C–Cl emission at 278.84 nm (peak b in Fig. 2) was determined by calculating the percent overlap of peak area of the emission profile. The emission intensity of the C–Cl band actually consists of only 3.1% of C_2 emission and this overlap was not studied in great detail. Within the concentration region studied, the C_2 overlap did not seriously vary from the 3.1% value determined; therefore, linearity was assumed for the region. The linear response of the ACPD can be attributed to C–Cl emission. However, the

overlap is significant enough to affect the detector selectivity towards C–Cl *versus* carbon. The C–Cl emission bands in other regions of the spectra, including the less intense band at 277.83 nm, yielded poorer S/N than the analytical band; C_2 overlap for these peaks were usually worse than 10% of the actual C–Cl emission intensity.

Detection limits

All ACPD parameters were set to their previously determined optima[23]. Calibration curves for DCD, TCE, DCB and NBC were constructed. In general, the linearity extended over 3 orders of magnitude. Some linearity was lost due to self-absorption at high concentrations and excessive background molecular emission interference at low concentrations. The correlation coefficients ranged from 0.995 to 0.999 for the compounds examined in the study, as listed in Table II. Detector reproducibility was determined by the long term relative standard deviation, over a three-week period. Typically, the reproducibility was 10% week to week. The detection limit is defined as the minimum mass that produces a response (peak area) that is twice that of the noise (peak area) at the retention time of the compound[10,28,29]. The mass in this case is represented by the C–Cl diatomic species. The detection limits and correlation coefficient values are listed in Table II.

Some experimental limitations did affect our detection limits and selectivity. First, although the light gathering power of the McPherson monochromator employed is quite high (f/7), the band emission of the C–Cl band is weak compared to atomic emission. The predominance of diatomic emission may be due to the fact that a.c.-arc plasma temperatures are comparatively lower than most other plasma temperatures[30]. Therefore, complete fragmentation is not achieved, even with the more energetic helium plasma. Finally, no attempt was made to reduce the background spectral interference caused by molecular emission. Techniques, such as lock-in amplifying, oscillating quartz plates incorporated within a monochromator and pulsed power sources, have previously been suggested and often lead to enhanced S/N and selectivity[31–33].

Selectivity and relative response

The maximum S/N for the C–Cl signal was obtained with a slit width of 1500 μm (bandpass 0.3 nm), as noted by the authors previously[23]. However, to reduce the inclusion of adjacent C_2 swan bands as part of the C–Cl response, the slit was reduced to 500 μm (bandpass 0.1 nm). The background that directly overlapped with the 278.84 nm C–Cl band could not be eliminated without seriously affecting the detector sensitivity due to a large decrease in energy throughput. The selectivity was established

TABLE II

DETECTION LIMITS FOR ORGANOCHLORINES STUDIED

Compound	*Detection limit (ng/s)*	*Correlation coefficient (r)*
Tetrachloroethylene	1.59	0.995
n-Butylchloride	1.12	0.998
p-Dichlorobenzene	1.53	0.999
1,10-Dichlorodecane	0.706	0.999

TABLE III

RELATIVE RESPONSE FACTORS (RRFs) FOR VARIOUS ALKYLCHLORIDES AND PHENYLCHLORIDES

Compound	*Number of carbon in backbone*	*No. of CCL moieties*	*RRF*
1-Chloropropane	3	1	1.21
n-Butylchloride	4	1	1.00
n-Pentylchloride	5	1	1.87
n-Hexylchloride	6	1	2.05
3-Chloromethylhexane	7	1	2.23
o-Chlorotoluene	7	1	2.56
p-Dichlorobenzene	6	2	3.73
1,6-Dichlorohexane	6	2	2.33
1,2,3-Trichloropropane	3	3	5.61
Tetrachloroethylene	2	4	3.55
1,10-Dichlorodecane	10	2	2.82

at 500 μm by injecting a 0.5-μl solution of DCD and dodecane at known concentrations. A known mass of C–Cl (representing DCD) and C_2 (representing dodecane) was introduced into the detector by adjusting the split ratio to 16.5/1 at a fixed flow-rate.

The selectivity is defined as the ratio of the peak area response of the ACPD towards C–Cl at 278.84 nm per gram of C–Cl to the peak area response of the ACPD towards C_2 originating from *n*-dodecane per gram of C_2[9]. In the presence of molecular background emission, the selectivity towards C–Cl was 24 under the GC/ACPD conditions employed, which agrees favorably with the selectivity values obtained with GC–MIP by McCormack *et al.*[26]. The selectivity of the ACPD towards C–Cl *versus* other molecular species, such as C–Br, CN and OH were then studied for potential interference. The values were calculated from the response towards standards of *p*-bromobenzene[11], dipropylamine[17] and *n*-octanol[15], representing C–Br, CN and

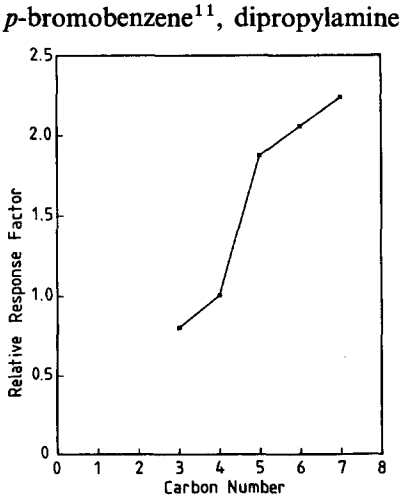

Fig. 3. Dependence of relative response factors on carbon number for chloro compounds containing one CCl per molecule.

OH, respectively. However, since the technique of GC–ACPD is a speciating technique, spectral interferences from these moieties are unlikely to be serious.

In order to study the effect of the molecular structure on the C–Cl response, a standard solution containing compounds of varying aromatic and aliphatic character were examined at known masses of C–Cl. Table III lists the relative response factors (RRFs) of the ACPD towards different organochlorine compounds, with *n*-butylchloride (NBC) being the internal standard. The relative response factor is defined as the mass of C–Cl in the sample compound per mass of C–Cl in NBC times the peak area of NBC to the peak area of the sample compound[34].

As seen in Table III, there is a complex trend that emerges with respect to the RRFs. Fig. 3 illustrates the overall increase in RRF with an increase of carbon number for *n*-alkylchlorides that produce one C–Cl entity per molecule of sample compound. This nonlinear increase is due to the enhancement in C_2 background emission with increasing carbon backbone. This phenomenon has been reported earlier in flame photometric detectors[35] and MIP[26] techniques. Examination of Table III reflects that in the case of *o*-chlorotoluene *versus* 3-chloromethylhexane counterpart with respect to carbon number and DCB *versus* its aliphatic counterpart 1,6-dichlorohexane, the aromatic ring introduces a larger contribution to the RRF than the alkane, probably because of the greater number of C_2 molecules produced per aromatic compound. Furthermore, TCE was expected to have a larger RRF than 1,2,3-trichloropropane (TCP). Since TCE contains only two carbons per molecule, only two C–Cl species can be formed per molecule compared to the three C–Cl that TCP can produce, thus TCP emission is greater than that of TCE emission.

Analytical applications

Several applications were performed in order to demonstrate the selectivity and stability that the ACPD exhibits to organochlorine compounds in complex matrices. First, a head space analysis was performed on a 1-ml mixture containing 1000 ng of the following organochlorine components in pentane: methylene chloride, chloroform, 1,2-dichloroethane, 1,3-dichloropropane, tetrachloroethylene, *p*-dichlorobenzene and 1,2,3-trichloropropane. Eluates of low k' values appear as sharp, well resolved peaks, as seen in Fig. 4. The chromatogram demonstrates that the ACPD introduces no detrimental effects on the separation, such as band broadening and memory effects as it compares favorably with a typical FID chromatographic profile of the same sample generated under similar conditions and with similar instrumentation. The slight decrease in base line is due to either self-absorption by a certain fragment present or the rapid decrease in the concentration of electrons caused by a species of high electron affinity. The latter would cause a decrease in plasma temperature and, therefore, a decrease in emission intensity[30].

A separation of a 1-μl aliquot of a 10-ml gasoline sample spiked with 10.72 mg of lindane was performed and is displayed in Fig. 5. The parallel chromatograms of the gasoline sample detected by both FID (A) and ACPD (B) under the same conditions clearly demonstrate the selectivity of the ACPD in a complex matrix. The high concentrations cause temperature fluctuations and self-absorption within the plasma, which leads to a lower background emission intensity and negative base line in certain regions. It should be noted that the hydrocarbons in the gasoline did not cause the plasma to extinguish. In fact, the base line became quite stable after, and in some cases

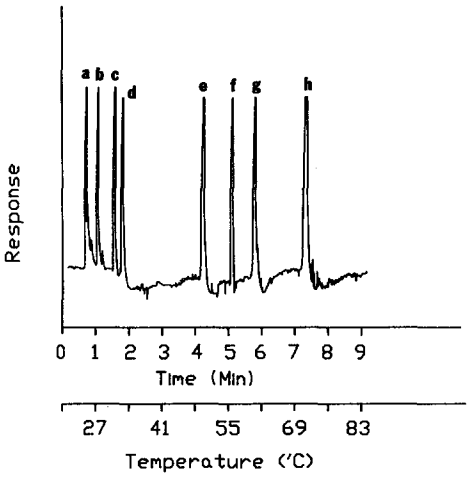

Fig. 4. Chromatogram of volatile organochlorine head space. GC conditions: column temperature 27°C (1 min) to 83°C at 7°C/min, 10 μl of vapor injected, injector split 5/1; column used was the DB-1 megabore column. (a) *n*-pentane; (b) methylene chloride; (c) chloroform; (d) 1,2-dichloroethane; (e) 1,3-dichloropropane; (f) tetrachloroethylene; (g) *p*-dichlorobenzene; (h) 1,2,3-trichloropropane.

during, the initial plasma cooling effect caused by these components.

Finally, a 10-ml aliquot of number 2 fuel oil was spiked with 10 mg of Aroclor 1254 and the parallel FID and ACPD chromatograms are displayed in Fig. 6a–c. Fig. 6a is the FID chromatogram of Aroclor 1254, which was run under the same conditions as the ACPD chromatogram of Aroclor 1254 in fuel oil (Fig. 6b). The ACPD chromatogram in Fig. 6b has more noise associated with it compared to Fig. 6a because diesel oil is also present, which leads to an increase in background emission. However, Fig. 6b demonstrates that the ACPD greatly simplifies the complex chromatogram of fuel oil and Aroclor 1254, shown in Fig. 6c, in addition to providing valuable qualitative information.

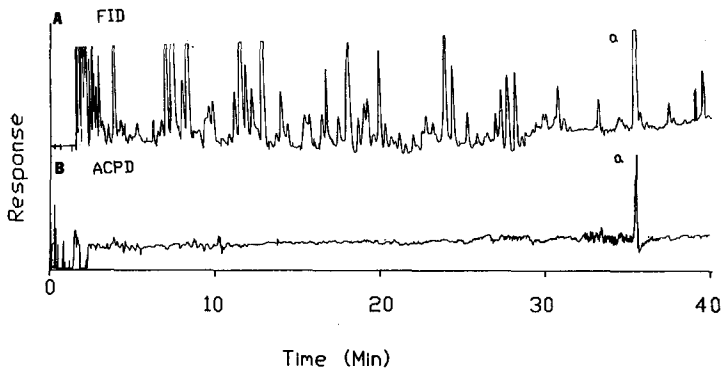

Fig. 5. (A) lindane (a) in gasoline detected by FID; GC conditions: 35°C (5 min) to 100°C at 4°C/min then to 230°C at 5°C/min on DB-1 megabore column. (B) lindane (a) in gasoline detected by ACPD, same GC conditions as above.

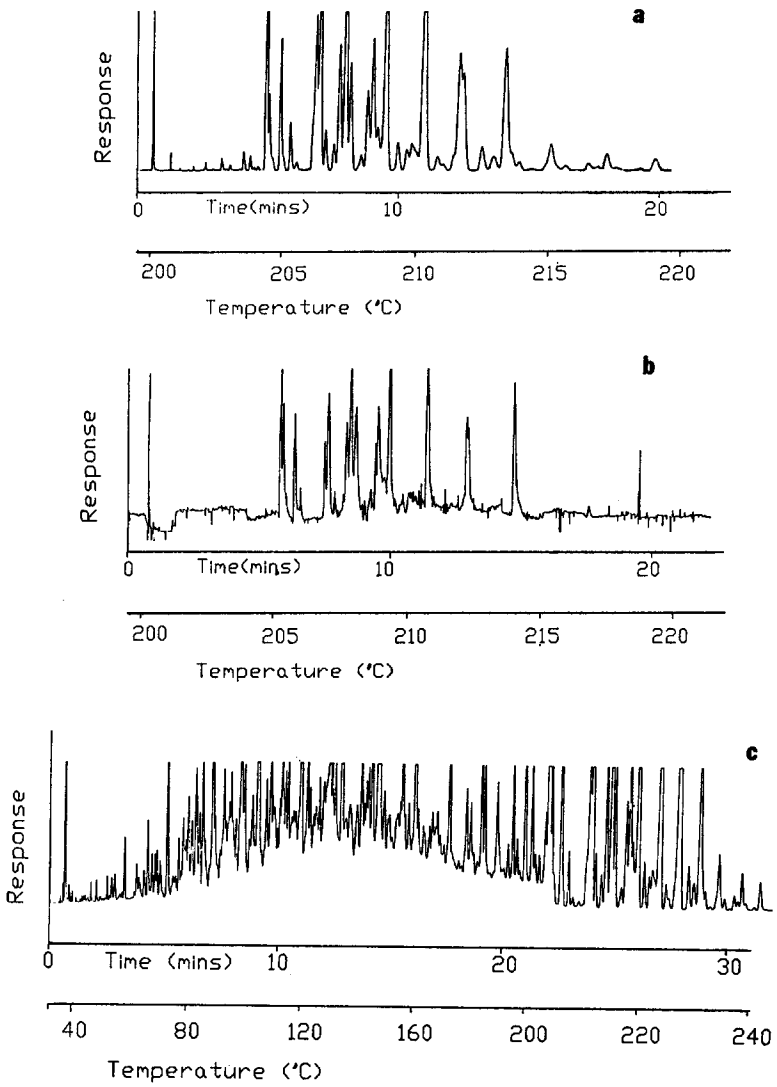

Fig. 6. (a) Aroclor 1254 detected by FID on the CP SIL-8 CB megabore column; GC conditions: 200°C (0.5 min) to 225°C at 1°C/min, 1 μl injection, injector split 5/1. (b) Aroclor 1254 in diesel gas detected by ACPD; same conditions as above. (c) Aroclor 1254 in diesel gas detected by FID; GC conditions: 40°C (1 min) to 200°C at 8°C/min then to 240°C at 4°C/min.

CONCLUSION

The alternating current plasma detector for capillary GC presented here offers considerable potential as a selective detector for organochlorine compounds, although detector sensitivity and selectivity are lower than those associated with GC–MIP techniques due to the experimental limitations. The RRFs show a complicated trend and a complete series of organochlorine compounds would have to be examined in

order to completely understand the complicated response dependency. However, it can be seen that two factors, aromatic character and carbon number, clearly contribute to the response of the detector.

In addition, the ACPD shows great potential in many applications of selective chlorine detection. The ACPD is a relatively inexpensive and simple detector to construct and operate. It circumvents many of the disadvantages assciated with MIP detection, such as solvent extinguishment and complicated interface venting devices. Detector selectivity for the diatomic C–Cl species did provide less complex chromatograms of a complex sample. Background correction devices and further filtering techniques will only improve the ACPD performance enough to be as popular as GC–MIP, with a simpler design. These modifications are currently being investigated and will be the subject of a future communication.

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