Applications using the chlorine-selective pulsed discharge emission detector

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Abstract

The use of the chlorine-selective pulsed discharge emission detector (Cl-PDED) for the GC analyses of EPA mixtures 502, 612, 624, organochlorine pesticides, and polychlorinated biphenyls has been demonstrated. The Cl-PDED is the most sensitive chlorine-selective detector with a minimum detectability of 50 fg Cl/s. A constant response/pg Cl was observed for these mixtures regardless of the number of Cl atoms/molecule and structure of the compound to which the Cl atoms are attached. The analysis of standard samples of polychlorinated biphenyls using the Cl-PDED have sensitivities comparable to those of the electron-capture detector; however, the predictable response/pg Cl from the Cl-PDED is preferred over the extremely variable response from the electron capture detector. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Detection, GC; Pulsed discharge emission detection; Krypton; Organochlorine compounds; Pesticides; Polychlorinated biphenyls; Chlorine selective detector

1. Introduction

In the preceding paper in this issue [1] the chlorine-selective pulsed discharge emission detector (Cl-PDED) was introduced. The effect of various parameters on the sensitivity, response factor and general performance of the detector were evaluated extensively. The Cl-PDED has a similar response factor (with a variation of 4.5%) for all chlorine atoms regardless of the nature of the molecule and a single calibration curve can be used to evaluate the response factor from the known empirical formula of the compound. The sensitivity of the detector was evaluated with a minimum detectability of ~50 fg Cl/s. The linear range of the detector is at least

2000. The selectivity with respect to carbon is ~1000, but since the carbon emission is principally in the form of stray light, the selectivity could be increased 3–4 orders of magnitude by using a double monochromator.

In this paper we wish to show the applications of this detector with emphasis on environmental analyses. In many of the applications an electron-capture detector (ECD) is used, but as was pointed out in the previous paper [1], the ECD response is highly sensitive to the structure of the molecule and the nature of the substituents, and the response factor for compounds can range up to ~10^6. If the goal is to detect Cl containing compounds, the Cl-PDED is preferable since the response per chlorine is constant and all compounds can be quantitatively analyzed with a single calibration curve. The sensitivity of the

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Cl-PDED is about 10 times less than the pulsed discharge electron-capture detector (PDECD) for compounds that are strong electron capturers such as CCl_4. On the other hand, for moderate or weak electron capturers, the Cl-PDED is much more sensitive than the PDECD.

In the present study the chromatogram using the Cl-PDED is compared with the chromatogram using the 193.1 nm carbon emission as a C-PDED. One may note that the relative responses for a compound reflects the relative abundance of Cl and C in the compound. However, the response from the carbon emission at 193.1 nm is far less than the KrCl* emission at 222 nm and the C-PDED is of marginal value. In the subsequent paper in this series [2] the Cl-PDED response is compared to the response from a more sensitive helium pulsed discharge photoionization detector (He-PDPID) and this is a more practical way of assessing the relative abundance of Cl to the other atoms in the molecule. This information is very useful in making a qualitative identification of the Cl-containing compound.

2. Experimental

The same Cl-PDED, pulse generator, spectrometer, and gas chromatograph as described in the previous paper [1] were used. The chromatographic conditions are shown in the chromatogram caption. All samples were liquids and were injected through the splitter. The temperature program used varied with the nature of the mixture injected. A J&W DB-5.625 capillary column 30 m×0.25 mm I.D., film thickness 0.5 μm was used for the analysis of volatile compounds; a J&W DB-5 ms capillary column 30 m×0.25 mm I.D., film thickness 0.25 μm was used for the analysis of US Environmental Protection Agency (EPA) mixture 612 chlorinated hydrocarbons, polychlorinated biphenyls (PCBs) and organochlorine pesticides.

The standard mixtures EPA 502 volatile 100 mixture, EPA 624 mixture without gases, EPA 612 chlorinated hydrocarbons, EPA 608 organochlorine pesticides and PCB congeners were purchased from NSI (NSI Environmental Solutions, Research Triangle Park, NC, USA). Purity of the other chemicals used in this study is above 99%.

3. Results and discussion

3.1. Volatile and semivolatile chlorinated compounds

In Fig. 1 the chromatogram of EPA 502 volatile 100 mix is shown using the Cl-PDED. A 10-pg amount of each of the components was injected and generally a good signal-to-noise ratio was obtained from the detector. The wide variation in response for each of the components in the mixture is primarily due to the Cl content. For example, peak 14 is dibromochloromethane and due to the large mass of bromine, the percent Cl is only 17%. Consequently, the peak height is low since only 0.68 pg of the 4 pg injection is Cl. On the other hand, peak 8 results from the elution of CCl_4 where the Cl percentage is 92.2%. Consequently, the peak height for CCl_4 is much greater than for $CHBr_2Cl$. Note in the chromatogram the generally good peak shape with little tailing. This reflects the small volume of the Cl-PDED and the small dead volume of the Tee at the inlet of the detector.

The quantitative results from the Cl-PDED for five consecutive chromatograms of the EPA 502 volatile 100 mixture are shown in Table 1. Note the good reproducibility of the peak areas giving a relative standard deviation (RSD) of <4% as shown in the last column. This is about the error expected from the syringe used to make the injections. The response/pg Cl is relatively constant with the exception of the three compounds eluted first. These are the most volatile and very likely there is some loss due to evaporation. The 14.9% variation in the response/pg Cl is higher than that observed in the previous study using mixtures prepared freshly in our laboratory [1].

Chromatograms for EPA 624 mix without gases are shown in Fig. 2. Fig. 2a shows the chlorine-selective detection at the KrCl* emission of 222.1 nm. For comparison the detection in the carbon emission mode in Fig. 2b was carried out at a wavelength 193.1 nm of the elemental carbon emission using the same detector with Kr-doped helium as the discharge reaction gas. The components of the mixture are listed in the figure caption. Again note the generally good peak shape for both modes of detection. The sensitivity using the elemental carbon
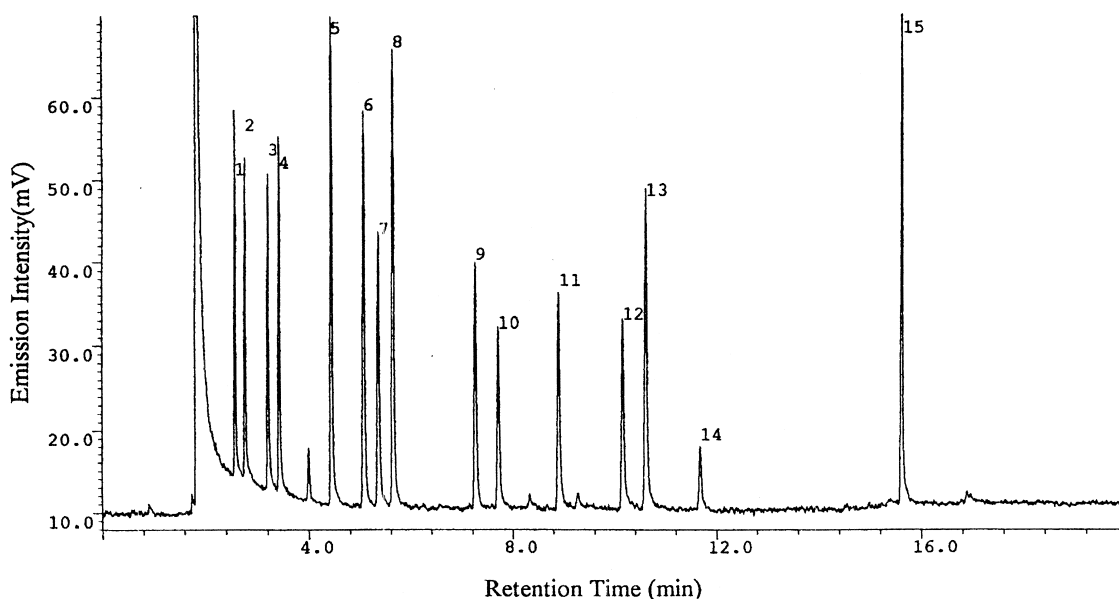
Fig. 1. Chromatogram of EPA 502 mixture using the Cl-PDED. Column: DB-5.625, 30 m×0.25 mm I.D., d_f: 0.5 μm, oven temperature program: 30°C (5 min), 5°C/min to 70°C, 20°C/min to 130°C (4 min), carrier gas: He, 30 cm/s, pulse width: 15 μs, pulse spacing: 400 μs, wavelength: 222.1 nm, discharge gas: 0.24% krypton in helium, flow-rate: 6 ml/min, detector temperature: 150°C, injector temperature: 200°C, injector split ratio: 86:1, 0.1 μl sample in methanol, 10 pg each. 1=1,1-Dichloroethene, 2=methylene chloride, 3=trans-1,2-dichloroethene, 4=1,1-dichloroethane, 5=chloroform, 6=1,1,1-trichloroethane, 7=1,2-dichloroethane, 8=carbon tetrachloride, 9=1,2-dichloropropane, 10=bromodichloromethane, 11=cis-1,3-dichloropropene, 12=trans-1,3-dichloropropene, 13=1,1,2-trichloroethane, 14=dibromochloromethane, 15=1,1,2,2-tetrachloroethane.

emission with the Kr-doped helium as the discharge reaction gas is much lower than the KrCl* emission, so a larger amount of material was injected, 225 pg/component, in order to get a chromatogram with a good signal-to-noise ratio. If pure helium was used as the discharge gas, the sensitivity in the elemental carbon emission mode was higher than with the Kr-doped helium, however, peaks eluting early were obscured by a large solvent peak. For this reason, the Kr-doped helium was used as the discharge gas in order to obtain a smaller solvent peak. The sample also contained benzene, toluene, and ethylbenzene in addition to the Cl-containing compounds. Benzene coelutes with peak 8, carbon tetrachloride. In the carbon emission mode at 193.1 nm the overlapped peak of benzene and carbon tetrachloride is much larger than peaks 5, 6, and 7 which reflects the added emission from benzene, as shown in Fig. 2b. However, in the KrCl* emission mode, response to carbon tetrachloride plus benzene appears to repre-

sent the Cl content of CCl_4 in comparison with peaks 5, 6, and 7 in Fig. 2a and is not influenced by the presence of the benzene. A similar situation occurs with (toluene and peak 13). Ethylbenzene does not coelute with the Cl-containing compounds. Its peak is quite obvious in the carbon emission mode but has no response in the KrCl* emission mode.

The quantitative results from the Cl-PDED for five consecutive chromatograms of the EPA 624 mixture without gases are given in Table 2. Again the reproducibility for each compound is 2~4%, as shown in the last column. The response/pg Cl is constant except for the first four compounds that are more volatile. Most likely evaporation of the volatile compounds is the reason for their lower response/pg Cl. The variation in response/pg Cl for all compounds is 12.4% and again higher than that observed in the previous study [1]. If the first four compounds are excluded, the average response/pg Cl from the remaining compounds is 32.25 mV s/pg Cl and the

Table 1
Elemental response of EPA 502 mixture

Compound name	Cl (%)	Cl[a] (pg)	Cl[b] (R/pg)	RSD[d] (%)
1,1-Dichloroethene	73.14	16.65	20.15	1.4
Methylene chloride	83.48	19.00	21.33	3.0
trans-1,2-Dichloroethene	73.14	16.65	21.70	1.0
1,1-Dichloroethane	71.65	16.31	27.38	1.3
Chloroform	89.08	20.27	30.34	3.2
1,1,1-Trichloroethane	79.72	18.14	31.01	3.2
1,2-Dichloroethane	71.65	16.31	27.40	3.0
Carbon tetrachloride	92.19	20.98	31.23	2.5
1,2-Dichloropropane	62.75	14.28	28.84	2.9
Bromodichloromethane	43.28	9.85	29.81	2.4
cis-1,3-Dichloropropene	63.89	14.54	24.44	2.7
trans-1,3-Dichloropropene	63.89	14.54	21.87	3.7
1,1,2-Trichloroethane	79.72	18.14	30.11	3.1
Dibromochloromethane	17.02	3.87	29.29	2.2
Tetrachloroethene	85.51	19.46	31.09	3.0
Average			27.07	
SD[c]			4.04	
RSD %[d]			14.92	

[a] Mass of chlorine injected.
[b] Average elemental response (mV s/pg Cl) calculated from five measurements.
[c] Standard deviation.
[d] Relative standard deviation.

RSD is 6.5%. This is still higher than that observed in the previous study using mixtures prepared freshly in our laboratory but much smaller than the 12.4%.

Fig. 3 shows chromatograms of the EPA 612 mixture to analyze semivolatile chlorinated hydrocarbons. A 50-pg amount of each of the compounds was injected for both chromatograms of Fig. 3. Fig. 3a shows the chlorine-selective detection at the KrCl* emission wavelength of 222.1 nm. For comparison in Fig. 3b the carbon detection at the carbon emission line of 193.1 nm using the same detector with pure helium as the discharge reaction gas is shown. The detector was operated at a temperature of 185°C and the final column temperature was 200°C. A stable baseline was observed with these chromatographic conditions.

The quantitative results for the five chromatograms of the EPA 612 mixture are shown in Table 3. The results are comparable to those in Tables 1 and 2 in terms of precision; the response/pg Cl is reasonably constant except for hexachlorobenzene. Very likely there is decomposition either before, or during

the analysis due to the heated metal Tee surface at the inlet of the Cl-PDED. Excluding the value for hexachlorbenzene, the average response/pg Cl is 13.6 with an RSD of 9.3%.

3.2. Polychlorinated biphenyls

PCBs are still major environmental pollutants because of their high stability and bioaccumulation potential [3]. The ECD is the most sensitive detector to PCBs [4]. However, the response of the ECD is dependent on the number of chlorine atoms and the structure of the PCBs [4]. Individual standards are required for all PCBs of interest in order to establish an accurate calibration curve. Since the total number of PCBs is 209 [3], the task of quantitative analysis of PCBs is complicated by ECD. Furthermore, the linearity of the ECD response for PCBs is poor. The atomic emission detector provides a uniform response per chlorine to PCBs [5,6]; however, its sensitivity with a minimum detectable amount of ~400 pg PCB [5,6] is low compared with the ECD. The Cl-PDED not only has much higher sensitivity (50 fg Cl/s) than the atomic emission detectors (4.4 pg Cl/s), but it also provides a uniform elemental response to the PCBs.

The chlorine-selective detection of PCB congeners using the KrCl* emission is shown in Fig. 4a. For comparison, the detection in the carbon emission mode at 193.1 nm using pure helium as the discharge reaction gas is shown in Fig. 4b. A 52-pg amount of each of seven PCBs was injected for both chromatograms. The Cl-PDED detector was operated at 185°C and the final column temperature was 240°C. A stable baseline in the KrCl* emission mode of Fig. 4a was observed even at the highest column temperature, which shows that the Cl-PDED is capable of detecting compounds eluted at this higher temperature. The greater noise in the baseline of the C-PDED emission at 193.1 nm is the result of running the C-PDED at a higher sensitivity level; i.e. the signal-to-noise level of Cl-PDED is much greater than that of the C-PDED.

The elemental responses to the seven PCBs are shown in Table 4. The response per chlorine for the Cl-PDED is uniform for the PCBs, regardless of the number of chlorine atoms and positions on the biphenyl skeleton. The data in Table 4 can be used to
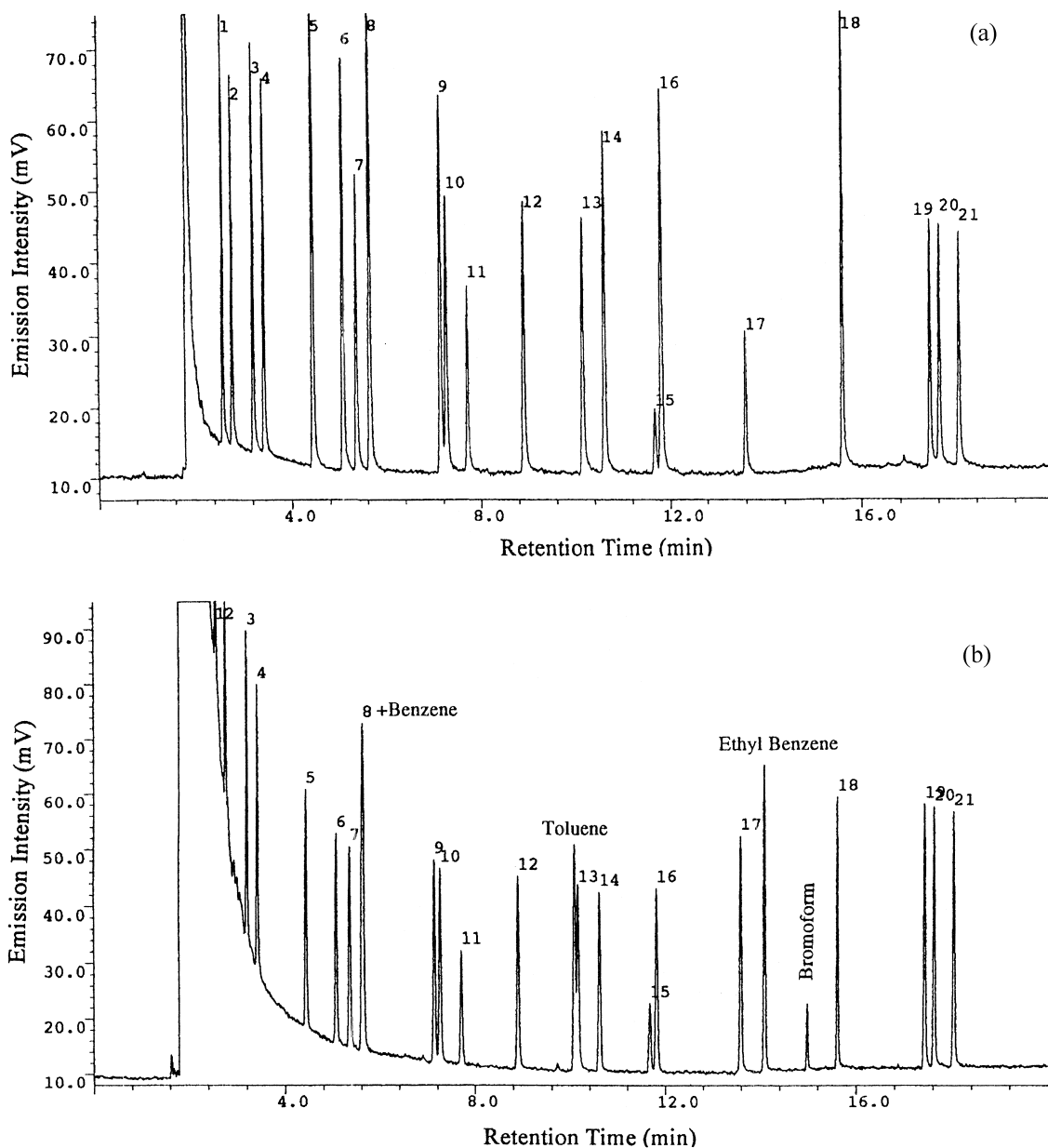
Fig. 2. (a) Chromatogram of EPA 624 mixture without gases using the Cl-PDED at KrCl* emission mode. Wavelength: 222.1 nm, column: DB-5.625, 30 m×0.25 mm I.D., d_f: 0.5 μm, oven temperature program: 30°C (5 min), 5°C/min to 70°C, 20°C/min to 130°C (4 min), carrier gas: He, 30 cm/s, pulse width: 15 μs, pulse spacing: 400 μs, discharge gas: 0.24% krypton in helium, flow-rate: 6 ml/min, detector temperature: 150°C, injector temperature: 200°C, injector split ratio: 86:1, 0.1 μl sample in methanol, 11 pg each. 1=1,1-Dichloroethene, 2=methylene chloride, 3=trans-1,2-dichloroethene, 4=1,1-dichloroethane, 5=chloroform, 6=1,1,1-trichloroethane, 7=1,2-dichloroethane, 8=carbon tetrachloride, 9=1,1,2-trichloroethene, 10=1,2-dichloropropane, 11=bromodichloromethane, 12=cis-1,3-dichloropropene, 13=trans-1,3-dichloropropene, 14=1,1,2-trichloroethane, 15=dibromochloromethane, 16=tetrachloroethene, 17=chlorobenzene, 18=1,1,2,2-tetrachloroethane, 19=1,3-dichlorobenzene, 20=1,4-dichlorobenzene, 21=1,2-dichlorobenzene. (b) Chromatogram of EPA624 mixture without gases using the Cl-PDED at carbon emission mode. Wavelength: 193.1 nm, 225 pg each.

Table 2
Elemental response of EPA 624 mixture

Compound name	M_r	No. of Cl	Cl (%)	Cl[a] (pg)	Cl[b] (R/pg)	RSD[d] (%)
1,1-Dichloroethene	96.94	2	73.14	15.28	21.38	2.6
Methylene chloride	84.93	2	83.49	17.45	22.28	2.9
trans-1,2-Dichloroethene	96.94	2	73.14	15.28	26.53	1.7
1,1-Dichloroethane	98.96	2	71.65	14.97	28.22	1.8
Chloroform	119.38	3	89.09	18.62	32.52	2.7
1,1,1-Trichloroethane	133.41	3	79.72	16.66	32.99	2.7
1,2-Dichloroethane	98.96	2	71.65	14.97	29.71	1.8
Carbon tetrachloride	153.82	4	92.19	19.27	35.21	2.6
1,1,2-Trichloroethene	131.39	3	80.95	16.92	32.82	2.7
1,2-Dichloropropane	112.99	2	62.75	13.11	36.64	3.4
Bromodichloromethane	163.83	2	43.28	9.04	33.85	4.1
cis-1,3-Dichloropropene	110.97	2	63.90	13.35	32.78	3.5
trans-1,3-Dichloropropene	110.97	2	63.90	13.35	30.08	3.0
1,1,2-Trichloroethane	133.41	3	79.72	16.66	33.71	3.6
Dibromochloromethane	208.29	1	17.02	3.56	31.00	2.8
Tetrachloroethene	165.83	4	85.52	17.87	34.13	1.5
Chlorobenzene	112.56	1	31.50	6.58	29.79	2.6
1,1,2,2-Tetrachloroethane	167.85	4	84.49	17.65	32.62	3.1
1,3-Dichlorobenzene	147	2	48.24	10.08	29.50	1.8
1,4-Dichlorobenzene	147	2	48.24	10.08	30.45	1.6
1,2-Dichlorobenzene	147	2	48.24	10.08	30.49	1.7
Average					30.80	
SD[c]					3.82	
RSD[d]					12.41	

[a] Mass of chlorine injected.
[b] Average elemental response (mV s/pg Cl) calculated from five measurements.
[c] Standard deviation.
[d] Relative standard deviation.

evaluate the precision of the elemental response for the PCBs. The RSD of the five measurements for each PCB ranges from 1.7 to 4.4%. The average response/pg Cl for all seven PCBs is 16.88 mV s/pg Cl with an average precision of 5.0% at a total detector flow-rate of 5.3 ml/min. Thus, the Cl-PDED facilitates the quantitative analysis of PCBs.

In this study we have used only standard samples of PCBs. Real world PCB analyses generally have sample matrices that commonly interfere with the PCB analysis. If the selectivity of the Cl-PDED is only 1000 then these sample matrices could have a significant effect on the Cl-PDED response. These should be evaluated after the selectivity of the Cl-PDED is significantly increased.

3.3. Organochlorine pesticides

The ECD is most sensitive to pesticides analysis

[7]. However, like the PCB analysis, the atomic emission detector is an alternative for pesticide analysis [6,8]. We explored the use of the Cl-PDED to analyze organochlorine pesticides. Chromatograms for 16 organochlorine pesticides in the KrCl* emission mode and in the elemental carbon emission mode at 193.1 nm are shown in Fig. 5a and b, respectively. In the carbon emission mode pure helium was used as the discharge reaction gas. The same chromatographic conditions as in the analysis of the PCBs were used. In Table 5 we show the elemental responses for all 16 organochlorine pesticides. Unlike the PCBs, which are thermally stable, some pesticides may be decomposed at high temperature. Note for some pesticides, especially 4,4′-DDT, that their elemental responses are relatively low. These pesticides may be decomposed when they come in contact with the surface of the heated metal Tee at the inlet of the detector. Some of them may be
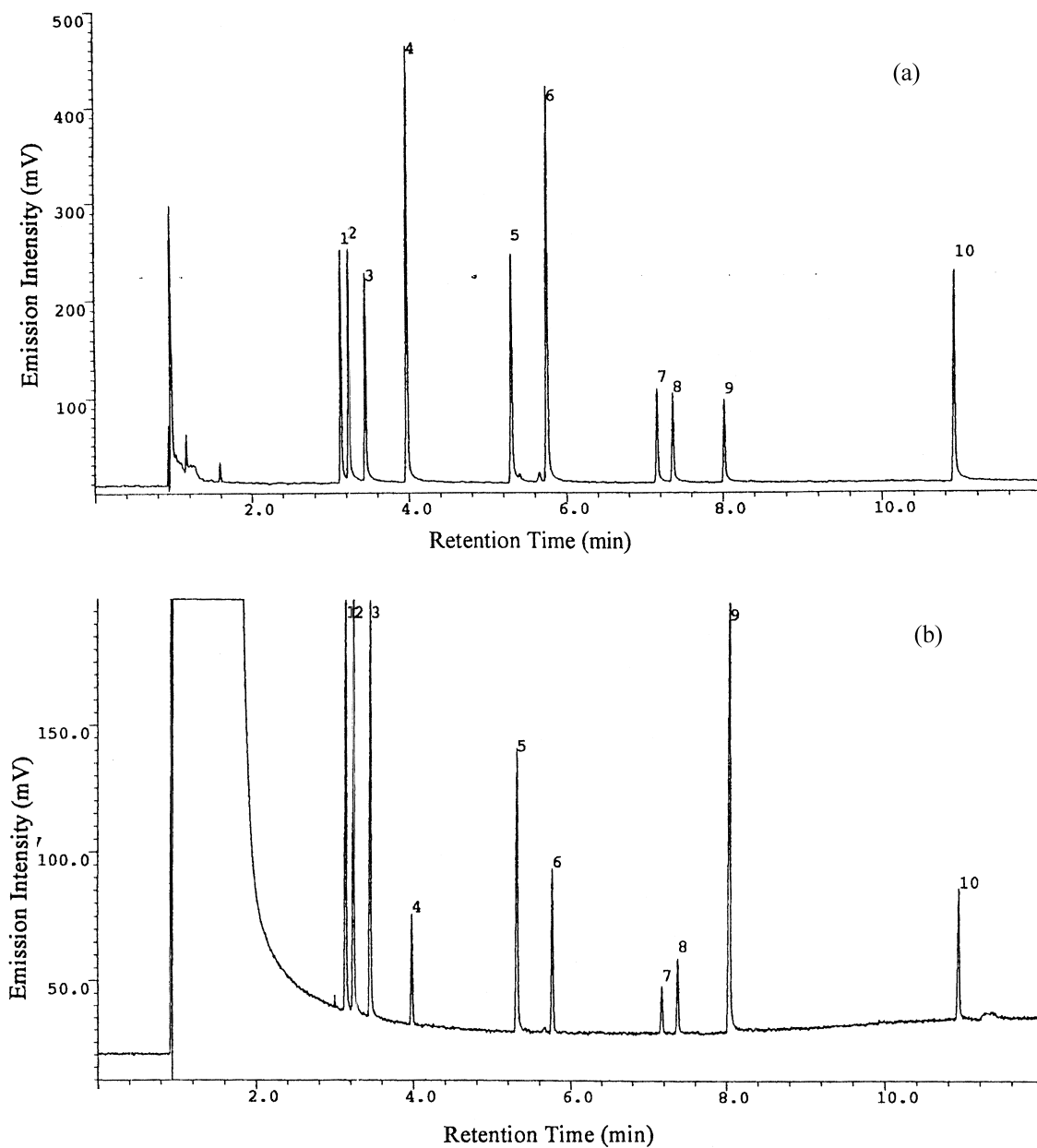
Fig. 3. (a) Chromatogram of EPA 612 mixture using the Cl-PDED at KrCl* emission mode. Wavelength: 222.1 nm, column: DB-5 ms, 30 m×0.25 mm I.D., d_f: 0.25 μm, oven temperature program: 80°C (1 min), 10°C/min to 140°C, 20°C/min to 200°C (2 min), carrier gas: He, 54 cm/s, pulse width: 15 μs, pulse spacing: 400 μs, discharge gas: 0.13% krypton in helium, flow-rate: 5.3 ml/min, detector temperature: 185°C, injector temperature: 300°C, injector split ratio: 38:1, 0.2 μl sample in methanol, 52 pg each. 1=1,3-Dichlorobenzene, 2=1,4-dichlorobenzene, 3=1,2-dichlorobenzene, 4=hexachloroethane, 5=1,2,4-trichlorobenzene, 6=hexachlorobutadiene, 7=unknown, 8=unknown, 9=2-chloronaphthalene, 10=hexachlorobenzene. (b) Chromatogram of EPA 612 mixture using the Cl-PDED at carbon emission mode. Wavelength: 193.1 nm, discharge gas: helium, flow-rate: 5.3 ml/min, 52 pg each.

Table 3
Elemental response of EPA 612 mixture

Compound name	M_r	No. of Cl	Cl (%)	Cl[a] (pg)	Cl[b] (R/pg)	RSD[d] (%)
1,3-Dichlorobenzene	147	2	48.24	25.14	12.34	2.0
1,4-Dichlorobenzene	147	2	48.24	25.14	13.61	3.5
1,2-Dichlorobenzene	147	2	48.24	25.14	12.50	3.5
Hexachloroethane	236.74	6	89.85	46.82	14.28	2.9
1,2,4-Trichlorobenzene	181.45	3	58.62	30.55	13.11	3.4
Hexachlorobutadiene	260.76	6	81.58	42.51	16.05	2.0
2-Chloronaphthalene	162.62	1	21.80	11.36	13.32	3.5
Hexachlorobenzene	284.78	6	74.70	38.92	10.08	0.8
Average					13.16	
SD[c]					1.71	
RSD%[d]					12.97	

[a] Mass of chlorine injected.

[b] Average elemental response (mV s/pg Cl) calculated from five measurements.

[c] Standard deviation.

[d] Relative standard deviation.

decomposed before analysis. The decomposition of the labile compounds will be improved by modification of the Cl-PDED to eliminate the metal surface exposed to the gas stream. Further studies are required to fully understand this phenomenon.

4. Conclusion

The Cl-PDED using the KrCl* emission at 222 nm has a constant response/mass chlorine and for this reason it is the preferred detector of volatile and semivolatile chlorine-containing compounds such as those in EPA 502, EPA 624, and EPA 612 mixtures. The Cl-PDED has a minimum detectability of 50 fg Cl/s, which is the same for all chlorine-containing compounds irrespective of structure and number of chlorine/molecule. On the other hand, the ECD is highly sensitive to compounds which contain a large number of Cl atoms on a single carbon, such as CCl_4, but is quite insensitive to compounds having only one or two Cl atoms on a single carbon [9].

Table 4
Elemental responses of PCBs

Compound name	M_r	No. of Cl	Cl (%)	Cl[a] (pg)	Cl[b] (R/pg)	RSD[d] (%)
2,4,4'-Trichlorobiphenyl	257.6	3	41.29	21.73	16.44	1.76
2,2',5,5'-Tetrachlorobiphenyl	292.0	4	48.57	25.56	18.29	3.38
2,2',4,5,5'-Pentachlorobiphenyl	326.4	5	54.31	28.58	17.30	1.60
2,3',4,4',5-Pentachlorobiphenyl	326.4	5	54.31	28.58	16.03	4.35
2,2',4,4',5,5'-Hexachlorobiphenyl	360.9	6	58.94	31.02	17.49	2.74
2,2',3,4,4',5'-Hexachlorobiphenyl	360.9	6	58.94	31.02	16.46	2.67
2,2',3,4,4',5,5'-Heptachlorobiphenyl	395.3	7	62.78	33.04	16.12	3.86
Average					16.88	
SD[c]					0.84	
RSD[d] (%)					4.97	

[a] Mass of chlorine injected.

[b] Average elemental response (mV s/pg Cl) calculated from five measurement

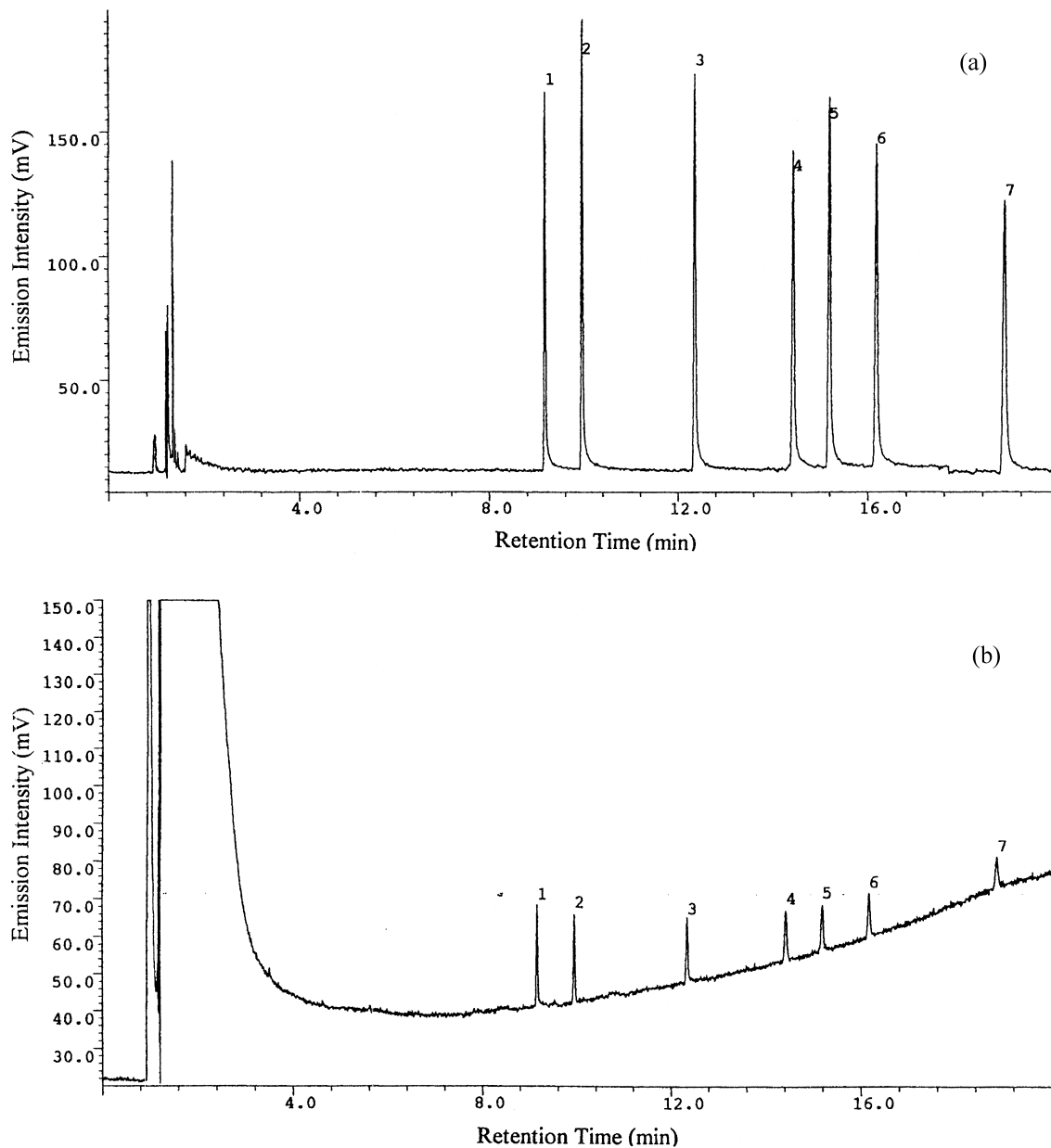[c] Standard deviation.

[d] Relative standard deviation.

Fig. 4. (a) Chromatogram of PCBs using the Cl-PDED at KrCl* emission mode. Wavelength: 222.1 nm, column: DB-5 ms, 30 m×0.25 mm I.D., d_f: 0.25 μm, oven temperature program: 80°C (1 min), 25°C/min to 190°C, 4°C/min to 240°C (2 min), carrier gas: He, 54 cm/s, pulse width: 15 μs, pulse spacing: 400 μs, discharge gas: 0.13% krypton in helium, flow-rate: 5.3 ml/min, detector temperature: 185°C, injector temperature: 300°C, injector split ratio: 38:1, 0.2 μl sample in methanol, 53 pg each. 1=2,4,4′-Trichlorobiphenyl, 2=2,2′,5,5′-tetrachlorobiphenyl, 3=2,2′,4,5,5′-pentachlorobiphenyl, 4=2,3′,4,4′,5-pentachlorobiphenyl, 5=2,2′,4,4′,5,5′-hexachlorobiphenyl, 6=2,2′,3,4,4′,5′-hexachlorobiphenyl, 7=2,2′,3,4,4′,5,5′-heptachlorobiphenyl. (b) Chromatogram of PCBs using the Cl-PDED at carbon emission mode. Wavelength: 193.1 nm, discharge gas: helium, flow-rate: 5.3 ml/min, 53 pg each.
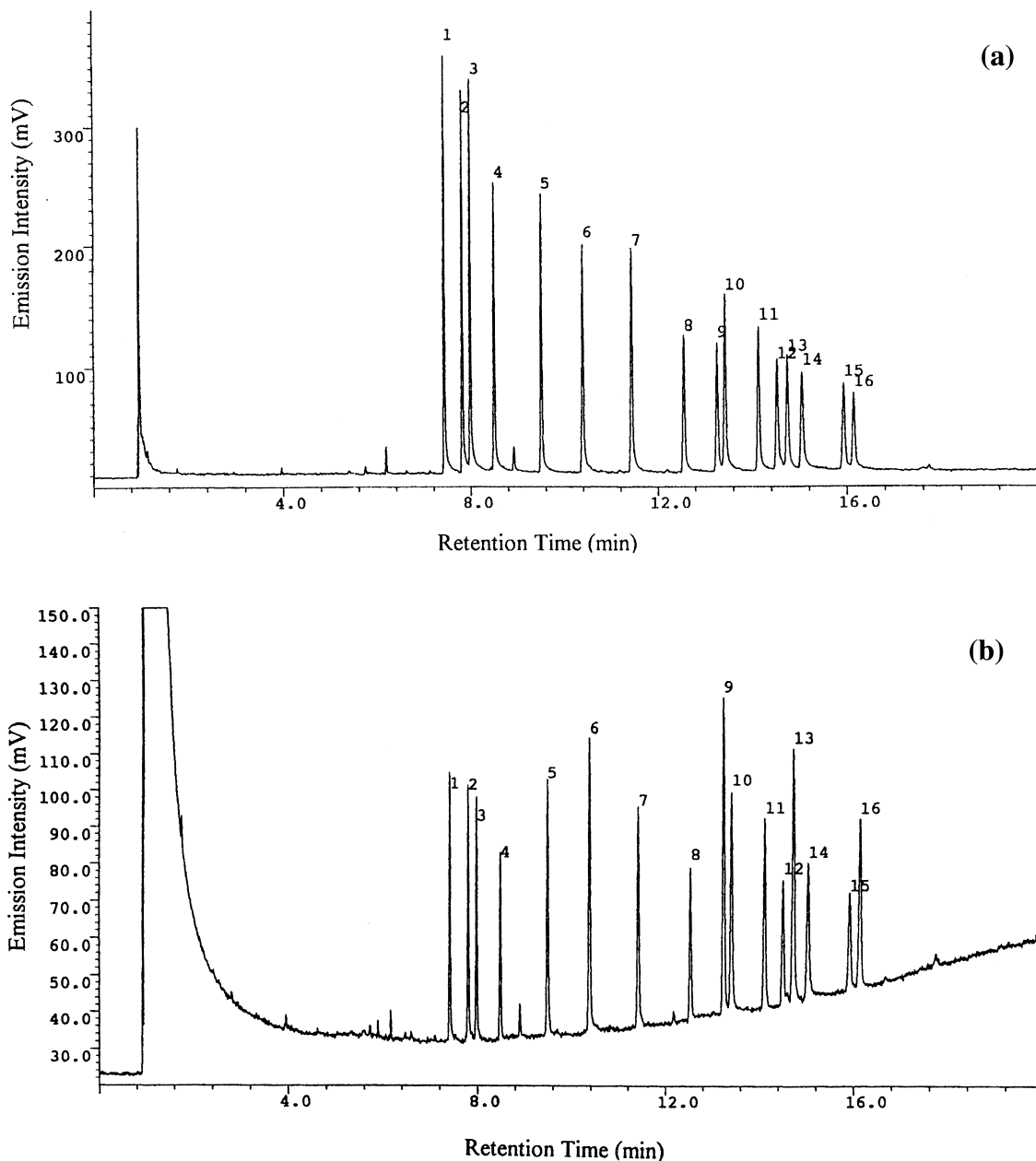
Fig. 5. (a) Chromatogram of organochlorine pesticides using the Cl-PDED at KrCl* emission mode. Wavelength: 222.1 nm, column: DB-5 ms, 30 m×0.25 mm I.D., d_f: 0.25 μm, oven temperature program: 80°C (1 min), 25°C/min to 190°C, 4°C/min to 240°C (2 min), carrier gas: He, 54 cm/s, pulse width: 15 μs, pulse spacing: 400 μs, discharge gas: 0.13% krypton in helium, flow-rate: 5.3 ml/min, detector temperature: 185°C, injector temperature: 300°C, injector split ratio: 38:1, 0.2 μl sample in methanol, 52 pg each. 1=α-BHC, 2=β-BHC, 3=γ-BHC, 4=δ-BHC, 5=heptachlor, 6=aldrin, 7=heptachlor epoxide, 8=endosulfan I, 9=4,4′-DDE, 10=dieldrin, 11=endrin, 12=endosulfan II, 13=4,4′-DDD, 14=endrin aldehyde, 15=endosulfan sulfate, 16=4,4′-DDT. (b) Chromatogram of organochlorine pesticides using the Cl-PDED at carbon emission mode. Wavelength: 193.1 nm, discharge gas: helium, flow-rate: 5.3 ml/min, 52 pg each.

Table 5
Elemental responses of organochlorine pesticides

Compound	M_r	No. of Cl	Cl (%)	Cl[a] (pg)	Cl[b] (R/pg)	RSD[d] (%)
α-BHC	290.83	6	0.7314	38.11	16.26	2.46
β-BHC	290.83	6	0.7314	38.11	15.39	3.18
γ-BHC	290.83	6	0.7314	38.11	16.49	2.60
δ-BHC	290.83	6	0.7314	38.11	13.40	2.39
Heptachlor	373.32	7	0.6647	34.64	14.48	3.77
Aldrin	364.9	6	0.5829	30.38	16.69	2.98
Heptachlor epoxide	389.32	7	0.6374	33.21	16.29	3.65
Endosulfan I	406.9	6	0.5227	27.24	13.28	2.79
4,4′-DDE	318.03	4	0.4459	23.23	14.45	2.17
Dieldrin	380.92	6	0.5584	29.10	16.62	3.85
Endrin	380.92	6	0.5584	29.10	13.42	2.26
Endosulfan II	406.9	6	0.5227	27.24	12.43	1.88
4,4′-DDD	320.05	4	0.4431	23.09	15.75	5.19
Endrin aldehyde	380.91	6	0.5584	29.10	11.75	4.80
Endosulfan sulfate	422.92	6	0.5029	26.21	11.23	5.06
4,4′-DDT	354.49	5	0.5000	26.06	9.66	6.01
Average					14.22	
SD[c]					2.17	
RSD (%)[d]					15.24	

[a] Mass of chlorine injected.
[b] Average elemental response (mV s/pg Cl) calculated from five measurements.
[c] Standard deviation.
[d] Relative standard deviation.

The analysis of PCBs can be performed with an ECD but the response is highly dependent upon the number of Cl substituents on the biphenyl structure. The electron capture coefficients can vary by over a factor of 100 when the number of Cl substituents varies from one to seven [10]. On the other hand, the Cl-PDED gives a uniform response/Cl and the variation in response/mol would range from 1 to 10, the maximum number of Cl substituents. The ECD response to PCBs varies with detector temperature, increasing with increasing detector temperature when there are 4 or fewer Cl substituents, and decreasing with increasing detector temperature when there are 5 or more Cl substituents. The ECD has greater sensitivity than the Cl-PDED when the number of Cl substituents is large (>6 Cl/molecule), but lower sensitivity than the Cl-PDED when the number of Cl atoms is less than 5 Cl/molecule.

The Cl-PDED can be used for organochlorine pesticide analysis but the sensitivity will not be as great as the ECD. The real advantage of Cl-PDED for organochlorine pesticide analysis is the elimina-tion of calibration factors, since the Cl-PDED response/Cl should be constant. The observed variations in response/pg Cl in Table 5 are most certainly due to decomposition prior to GC analysis or during GC analysis. This is especially true for 4,4′-DDT which is quite prone to thermal decomposition.

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