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Characterization of chlorinated compounds using a dual chlorine-selective pulsed discharge emission detector–helium-pulsed discharge photoionization detector system

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Abstract

The Cl-selective pulsed discharge emission detector (Cl-PDED) response is dependent only upon the Cl content, irrespective of the molecular structures of the compounds. This provides a simple, fast quantitative method of analysis for chlorinated compounds. The response of the helium-pulsed discharge photoionization detector (He-PDPID) is a function of the molecular structure and the number of photoionizable electrons using the He₂ band at 13.5–17.5 eV. The ratio of the responses of the two detectors is independent of concentration and can be used to characterize the Cl-containing compounds along with the retention time, or the ratio can be used as evidence for coelution. The dual Cl-PDED–He-PDPID detector system is a useful tool for peak identification. The effect of coeluting hydrocarbons on the Cl-PDED response was evaluated by spiking a gasoline sample with US Environmental Protection Agency mixture 502. All Cl-PDED responses were greater than 90% of the response in the absence of the hydrocarbons. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In previous papers in this issue [1,2] the chlorine-selective pulsed discharge emission detector (Cl-PDED) was introduced as the most sensitive chlorine selective detector. Applications using the Cl-PDED for the GC analyses of US Environmental Protection Agency (EPA) mixtures 502, 612, 624, organochlorine pesticides, and polychlorinated phenyls were demonstrated. The Cl-PDED has a minimum detectability of approximately 50 fg Cl/s for chlorinated

compounds, and a similar elemental response factor for all chlorinated compounds regardless of the nature of the molecule; a single calibration curve can be used for the quantitative analysis.

In gas chromatography there has always been a need for peak identification. Mass spectrometry and Fourier transform IR spectrometry are the most useful tools for peak identification. The use of four detectors has also been proposed to identify the GC peaks: He-PDPID, Ar-PDPID, Kr-PDPID and FID [3]. In the previous study [2] the relative abundance of Cl and C in a chlorinated compound reflected by the relative responses of the Cl-PDED response and

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the carbon-PDED response for the compound was observed. However, the sensitivity of the carbon-PDED at 193.1 nm is far less than the Cl-PDED, and a more sensitive detector should be used to compare the response from the highly sensitive Cl-PDED.

In this study we explored the use of the Cl-PDED combined with the helium pulsed discharge photoionization detector (He-PDPID) to characterize chlorinated compounds. The response of the Cl-PDED is dependent only on the Cl content [1], independent of molecular structures of compounds, which facilitates the quantitative analysis to chlorinated compounds. The response of the He-PDPID is a function of the molecular structure and the number of photoionizable electrons using the He₂ band at 13.5–17.5 eV [4–6]. The ratio of the responses of the two detectors along with the retention time can be used to characterize the chlorinated compounds.

The quenching of the Cl-PDED response by hydrocarbons was investigated in this study. This was done by spiking a gasoline sample with an EPA mixture 502.

2. Experimental

The same Cl-PDED described in previous papers [1,2] was used. The He-PDPID used in this work is a commercial detector (Valco, Houston, Texas, USA). The parallel Cl-PDED and He-PDPID detection was accomplished by splitting the column effluent into the two detectors with a fused-silica splitter (Supelco, Bellefonte, PA, USA). The column exit split ratio can be adjusted by changing the relative resistance of two exit gas streams from the splitter. Since the He-PDPID response to chlorinated compounds is lower than the Cl-PDED, the splitter ratio of the He-PDPID to the Cl-PDED was set to 7: 1 in favor of the He-PDPID in order to obtain adequate peak heights from the He-PDPID. The chromatographic conditions are given in the chromatogram caption. The standard EPA 502 volatile 100 mixture and EPA 624 mixture without gases were purchased from NSI (NSI Environmental Solutions, Research Triangle Park, NC, USA). Purity of other chemicals used in this study is above 99%.

3. Results and discussion

Chromatograms of a mixture of eight chlorinated compounds obtained using the parallel Cl-PDED and He-PDPID detection are shown in Fig. 1. In Figs. 2 and 3 we show chromatograms of the EPA 502 and EPA 624 mixtures, respectively. Since the exit resistance of the Cl-PDED is greater than the He-PDPID, the retention times in the Cl-PDED chromatogram are slightly longer than the He-PDPID. The He-PDPID is a universal detector, and it responds to both chlorinated compounds and non-chlorinated compounds, as shown in Fig. 3b. In Fig. 3 the sample contained benzene, toluene, and ethylbenzene in addition to the chlorinated compounds. The benzene coelutes with peak 8, carbon tetrachloride. In the He-PDPID chromatogram of Fig. 3b the overlapped peak of carbon tetrachloride and benzene is much larger than peaks 5, 6, and 7 which reflects the added signal from benzene. However in the Cl-PDED chromatogram of Fig. 3a the response to the overlapped peak appears to represent the Cl content of CCl₄ in comparison with peaks 5, 6, and 7 and is not influenced by the presence of the benzene. A similar situation occurs with the partly overlapped peak of toluene and peak 13, *trans*-1,3-dichloropropene. Ethylbenzene and bromoform in the He-PDPID chromatogram do not coelute with the chlorinated compounds, and again have no response in the Cl-PDED.

In Table 1 we give results for three mixtures in terms of ratios of Cl-PDED responses to the He-PDPID. The standard deviation is calculated from five measurements. The ratio $R_{\text{Cl-PDED/He-PDPID}}$ is calculated by Eq. (1)

$$\begin{aligned} R_{\text{Cl-PDED/He-PDPID}} &= \frac{\left(\frac{R_i}{R_{\text{st}}}\right)_{\text{Cl-PDED}}}{\left(\frac{R_i}{R_{\text{st}}}\right)_{\text{He-PDPID}}} \\ &= \frac{(R_i)_{\text{Cl-PDED}}}{(R_i)_{\text{He-PDPID}}} \bigg/ \frac{(R_{\text{CHCl}_3})_{\text{Cl-PDED}}}{(R_{\text{CHCl}_3})_{\text{He-PDPID}}} \end{aligned} \quad (1)$$

where R_{st} is the response of the internal standard, R_{CHCl_3} is the response of chloroform used as the

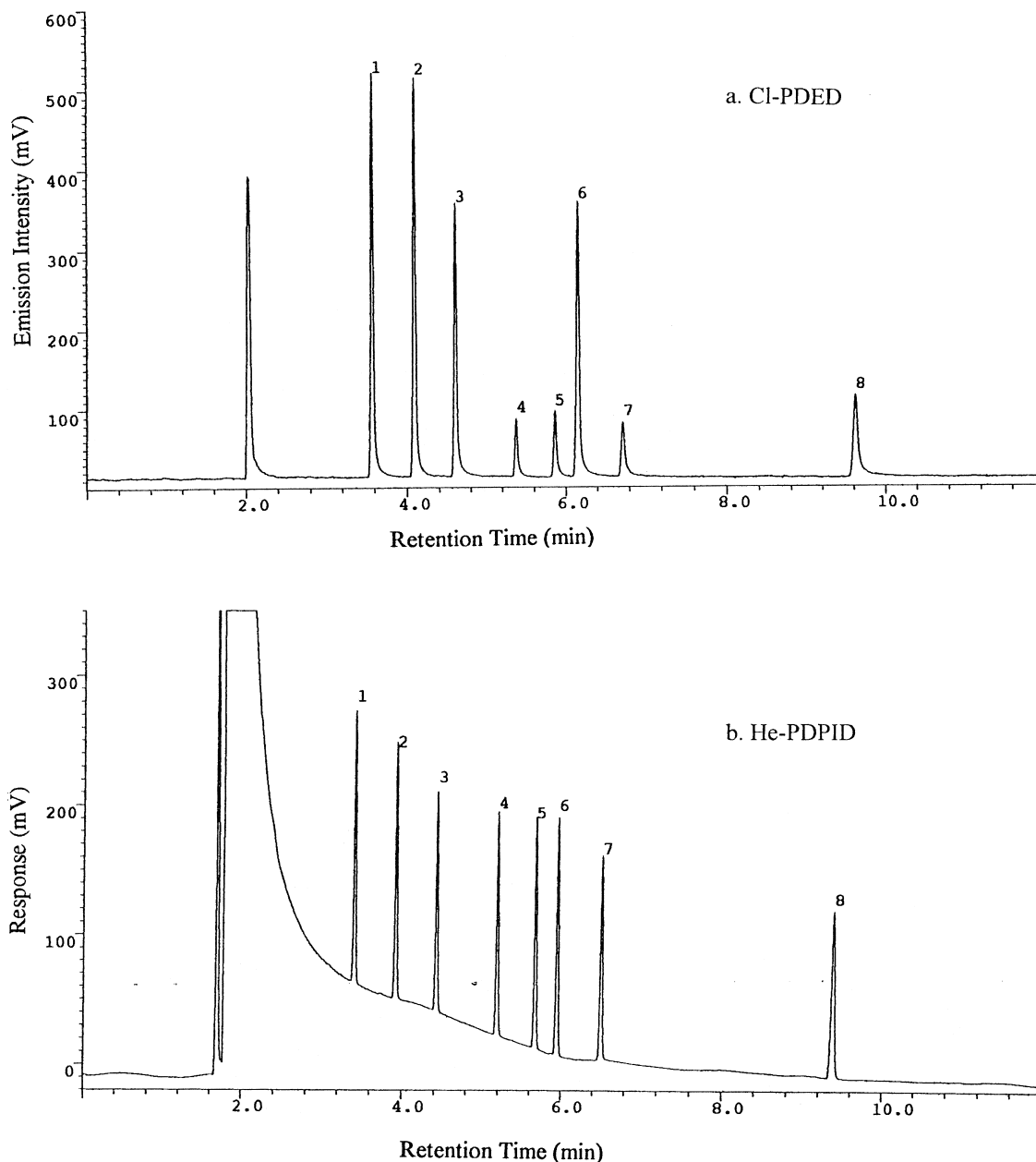


Fig. 1. Chromatograms of eight chlorinated compound mixture using parallel CI-PDED–He-PDPID detectors. Column: DB-5.625, 30 m \times 0.25 mm I.D., d_f : 0.5 μ m, column exit split ratio (He-PDPID/CI-PDED): 7:1, carrier gas: He, 30 cm/s, oven temperature program: 40 $^{\circ}$ C (2 min), 20 $^{\circ}$ C/min to 130 $^{\circ}$ C (5.5 min), injector temperature: 200 $^{\circ}$ C, injector split ratio: 100:1, 0.2 μ l sample in methanol. (a) CI-PDED. Pulse width: 15 μ s, pulse spacing: 400 μ s, wavelength: 222.1 nm, discharge gas: 0.20% krypton in helium, 3.5 ml/min, detector temperature: 130 $^{\circ}$ C. 1=Chloroform (34.26 pg), 2=carbon tetrachloride (37.15 pg), 3=trichloroethylene (33.98 pg), 4=1-chloropentane (20.50 pg), 5=cyclopentyl chloride (23.36 pg), 6=tetrachloroethylene (37.73pg), 7=chlorobenzene (25.87 pg), 8=1,2-dichlorobenzene (30.34 pg). (b) He-PDPID; discharge gas: He, 30 ml/min, detector temperature: 200 $^{\circ}$ C. 1=Chloroform (239.82 pg), 2=carbon tetrachloride (260.05 pg), 3=trichloroethylene (237.86 pg), 4=1-chloropentane (143.5 pg), 5=cyclopentyl chloride (163.52 pg), 6=tetrachloroethylene (264.11 pg), 7=chlorobenzene (181.09 pg), 8=1,2-dichlorobenzene (212.38 pg).

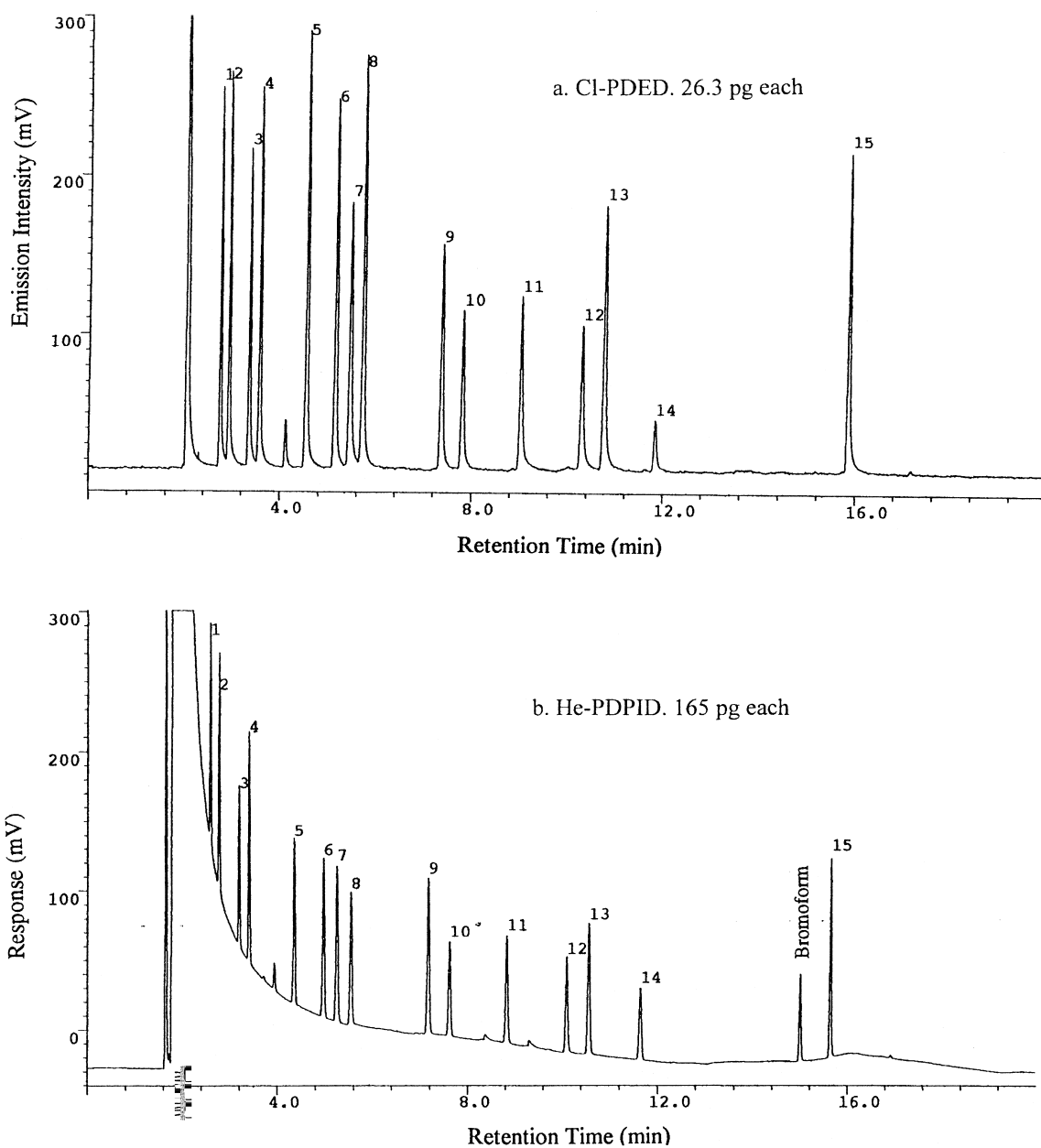


Fig. 2. Chromatograms of EPA 502 mixture using parallel CI-PDED–He-PDPID detectors. Column: DB-5.625, 30 m×0.25 mm I.D., d_f : 0.5 μ m, column exit split ratio (He-PDPID/CI-PDED): 7:1, carrier gas: He, 30 cm/s, oven temperature program: 30°C (5 min), 5°C/min to 70°C, 20°C/min to 130°C (4 min), injector temperature: 200°C, injector split ratio: 100:1, 0.2 μ l sample in methanol. (a) CI-PDED. Pulse width: 15 μ s, pulse spacing: 400 μ s, wavelength: 222.1 nm, discharge gas: 0.20% krypton in helium, 3.5 ml/min, detector temperature: 130°C. 23.6 pg each. (b) He-PDPID. Discharge gas: He, 30 ml/min, detector temperature: 200°C. 165 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.

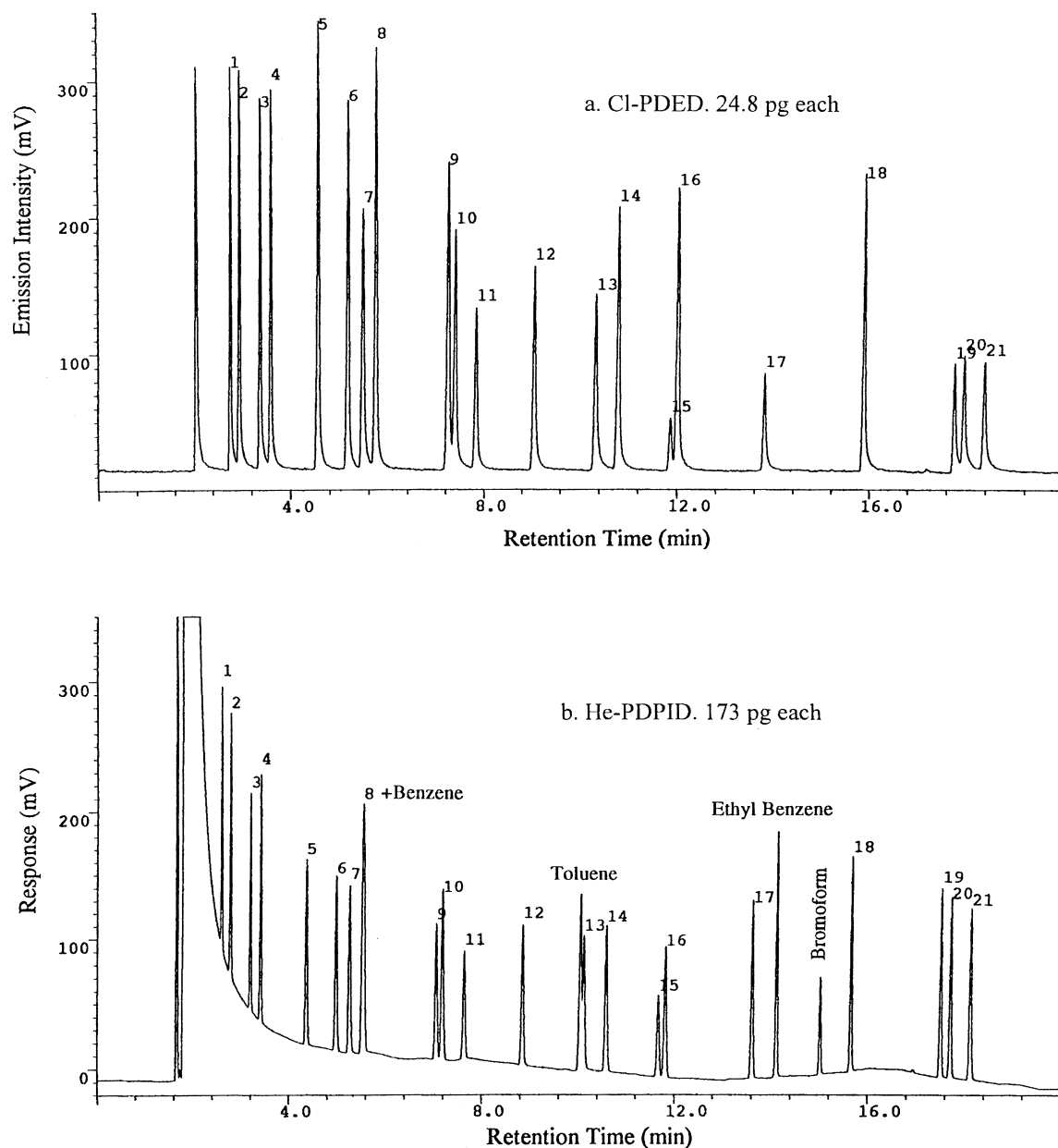


Fig. 3. Chromatograms of EPA 624 mixture without gases using parallel CI-PDED–He-PDPID detectors. Column: DB-5.625, 30 m \times 0.25 mm I.D., d_r : 0.5 μ m, column exit split ratio (He-PDPID/CI-PDED): 7:1, carrier gas: He, 30 cm/s, oven temperature program: 30 $^{\circ}$ C (5 min), 5 $^{\circ}$ C/min to 70 $^{\circ}$ C, 20 $^{\circ}$ C/min to 130 $^{\circ}$ C (4 min), injector temperature: 200 $^{\circ}$ C, injector split ratio: 100:1, 0.2 μ l sample in methanol, (a) CI-PDED. Pulse width: 15 μ s, pulse spacing: 400 μ s, wavelength: 222.1 nm, detector gas: 0.20% krypton in helium, 3.5 ml/min, detector temperature: 130 $^{\circ}$ C, 24.8 pg each. (b) He-PDPID. Discharge gas: He, 30 ml/min, detector temperature: 200 $^{\circ}$ C. 173 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.

Table 1
Ratios of Cl-PDED responses to He-PDPID responses

Compounds	M_r	No. of Cl	EPA 624 mixture		EPA 502 mixture		Mixture 8 ^c		Average
			Ratio ^a	SD ^b	Ratio	SD	Ratio	SD	
1,1-Dichloroethene	96.94	2	0.722	0.011	0.729	0.038	X ^d	X	0.726
Methylene chloride	84.93	2	0.752	0.007	0.753	0.035	X	X	0.752
<i>trans</i> -1,2-Dichloroethene	96.94	2	0.796	0.012	0.810	0.047	X	X	0.803
1,1-Dichloroethane	98.96	2	0.681	0.012	0.686	0.017	X	X	0.684
Chloroform	119.38	3	1.000	X	1.000	X	1.000	X	1.000
1,1,1-Trichloroethane	133.41	3	0.836	0.010	0.843	0.023	X	X	0.839
1,2-Dichloroethane	98.96	2	0.678	0.007	0.679	0.025	X	X	0.678
Carbon tetrachloride	153.82	4	X	X	1.100	0.044	1.006	0.014	1.053
Carbon tetrachloride + benzene	153.82 + 78.11		0.478	0.006	X	X	X	X	X
1,1,2-Trichloroethene	131.39	3	0.874	0.017	X	X	0.861	0.011	0.867
1,2-Dichloropropane	112.99	2	0.604	0.014	0.550	0.010	X	X	0.577
Bromodichloromethane	163.83	2	0.602	0.020	0.619	0.019	X	X	0.619
<i>cis</i> -1,3-Dichloropropene	110.97	2	0.632	0.007	0.672	0.025	X	X	0.672
Toluene	92.14	0	0.000	X	X	X	X	X	X
<i>trans</i> -1,3-Dichloropropene	110.97	2	0.568	0.012	0.598	0.015	X	X	0.583
1,1,2-Trichloroethane	133.41	3	0.727	0.015	0.728	0.029	X	X	0.727
Dibromochloromethane	208.29	1	0.239	0.005	0.266	0.008	X	X	0.252
Tetrachloroethene	165.83	4	0.883	0.009	0.723	0.018	0.855	0.012	0.821
Chlorobenzene	112.56	1	0.263	0.011	X	X	0.245	0.004	0.254
Ethylbenzene	106.17	0	0.000	X	X	X	X	X	X
Bromoform	252.75	0	0.000	X	0.000	X	X	X	X
1,1,2,2-Tetrachloroethane	167.85	4	0.703	0.007	X	X	X	X	0.703
1,3-Dichlorobenzene	147.0	2	0.298	0.004	X	X	X	X	0.298
1,4-Dichlorobenzene	147.0	2	0.317	0.003	X	X	X	X	0.317
1,2-Dichlorobenzene	147.0	2	0.316	0.004	X	X	0.362	0.011	0.339
1-Chloropentane	106.6	1	X	X	X	X	0.201	0.005	0.201
Cyclopentyl chloride	104.58	1	X	X	X	X	0.216	0.005	0.216

^a Average ratio of Cl-PDED response to He-PDPID response calculated from five measurements.

^b Standard deviation.

^c Mixture of eight compounds.

^d X, not contained in the mixture.

internal standard and R_i is the response of individual components.

Obviously, ratios for toluene, ethylbenzene and bromoform are zero since they have no responses in the Cl-PDED. The ratio of the overlapped peak of carbon tetrachloride and benzene drops dramatically to 0.478 due to the added signal from benzene in the He-PDPID, compared with the ratio of carbon tetrachloride of 1.100. These results would be helpful for peak identification, or can be used as evidence for coelution of a chloro containing compound and a non-chloro containing compound.

In order to obtain an understanding of the ratio of responses of the Cl-PDED to the He-PDPID we can

obtain an estimate of the responses based upon molecular composition. The response of the He-PDPID depends upon the number of electrons in orbitals with binding energies less than the energy of the He₂ emission from the discharge [6]. For a hydrocarbon chain the response to the He-PDPID has been shown to be roughly proportional to the number of carbons [4]. Chlorine has a higher atomic number than carbon, but also has the additional electrons in the valence shell. To a first approximation we can assume that the Cl and C atoms make similar contributions to the He-PDPID response. If we assume the chloro containing compounds contain only carbon and chlorine, we can assume the He-

PDPID response is proportional to the total number of C and Cl atoms in the molecule. Bromine has a much higher atomic number than carbon, containing electrons in the 4p orbitals. The response to bromine is approximately twice that of C or Cl. For chloro containing compounds which also contain Br we may assume the He-PDPID response to be proportional to the C+Cl atoms plus twice the number of Br atoms. Of course the Cl-PDED response is precisely proportional to the number of Cl atoms so the ratio of responses would be expected to be

$$\frac{R_{\text{Cl-PDED}}}{R_{\text{He-PDPID}}} = \frac{\text{No. of Cl}}{\text{No. of Cl} + \text{No. of C} + 2(\text{No. of Br})} \quad (2)$$

Since our ratio of responses is made relative to an internal standard, we must also divide by this ratio for the internal standard. For this study we have chosen CHCl_3 as the internal standard, and the ratio for CHCl_3 would be

$$\begin{aligned} & \frac{(R_{\text{CHCl}_3})_{\text{Cl-PDED}}}{(R_{\text{CHCl}_3})_{\text{He-PDPID}}} \\ &= \frac{\text{No. of Cl}}{\text{No. of Cl} + \text{No. of C} + 2(\text{No. of Br})} = \frac{3}{1+3} \\ &= \frac{3}{4} \end{aligned} \quad (3)$$

The estimated ratio, F_{Cl} , would then be given by Eq. (4)

$$F_{\text{Cl}} = \frac{\text{No. of Cl}}{\text{No. of Cl} + \text{No. of C} + 2(\text{No. of Br})} / (3/4) \quad (4)$$

where No. of Cl, No. of C and No. of Br are the numbers of Cl, C, and Br atoms in the molecule, respectively. The results are given in Table 2.

In Fig. 4 we show a graph of the estimated ratio as given by Eq. (4) versus the experimentally determined ratio. Note that there is a reasonably good fit

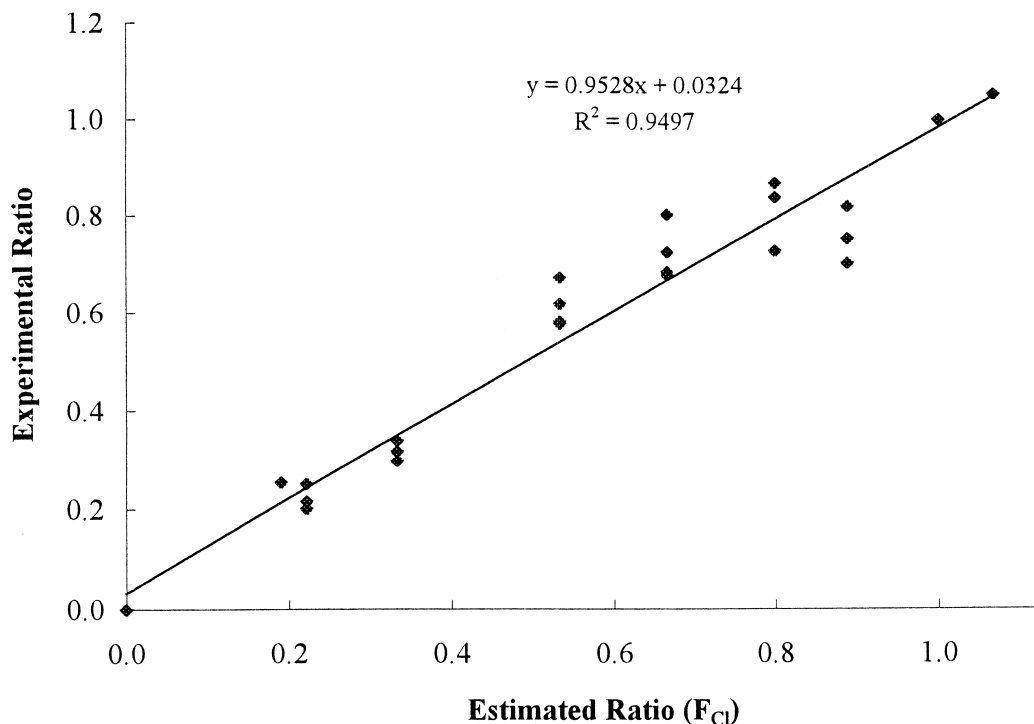


Fig. 4. Experimental ratio versus estimated ratio.

Table 2
Experimental ratio versus estimated ratio

Compounds	M_r	No. of Cl	No. of atoms ^a	F_{Cl} ^b	R_{exp} ^c
Toluene	92.14	0	6	0.000	0.000
Ethylbenzene	106.17	0	8	0.000	0.000
Bromoform	252.75	0	7	0.000	0.000
Chlorobenzene	112.56	1	7	0.190	0.254
Dibromochloromethane	208.29	1	6	0.222	0.252
1-Chloropentane	106.6	1	6	0.222	0.201
Cyclopentyl chloride	104.58	1	6	0.222	0.216
1,3-Dichlorobenzene	147.0	2	8	0.333	0.298
1,4-Dichlorobenzene	147.0	2	8	0.333	0.317
1,2-Dichlorobenzene	147.0	2	8	0.333	0.339
1,2-Dichloropropane	112.99	2	5	0.533	0.577
Bromodichloromethane	163.83	2	5	0.533	0.619
<i>cis</i> -1,3-Dichloropropene	110.97	2	5	0.533	0.672
<i>trans</i> -1,3-Dichloropropene	110.97	2	5	0.533	0.583
1,1-Dichloroethene	96.94	2	4	0.667	0.726
<i>trans</i> -1,2-Dichloroethene	96.94	2	4	0.667	0.803
1,1-Dichloroethane	98.96	2	4	0.667	0.684
1,2-Dichloroethane	98.96	2	4	0.667	0.678
1,1,1-Trichloroethane	133.41	3	5	0.800	0.839
1,1,2-Trichloroethene	131.39	3	5	0.800	0.867
1,1,2-Trichloroethane	133.41	3	5	0.800	0.727
Methylene chloride	84.93	2	3	0.889	0.752
Tetrachloroethene	165.83	4	6	0.889	0.821
1,1,2,2-Tetrachloroethane	167.85	4	6	0.889	0.703
Chloroform	119.38	3	4	1.000	1.000
Carbon tetrachloride	153.82	4	5	1.067	1.053

^a No. of Cl+No. of C+2(No. of Br).

^b Estimated ratio.

^c Experimental value.

considering the approximation made for the estimated value. The greatest deviations are for CH₂Cl₂ and 1,1,2,2-tetrachloroethane.

This type of correlation is also useful in categorizing an unknown compound that can not be identified by its retention time and relative response of the Cl-PDED–He-PDPID. From the ratio and the correlation given in Fig. 4, one can obtain an estimate of the ratio of Cl atoms to the total atoms in the molecule. This may suggest possibilities for the unknown compound, or evidence for coelution.

Finally, we show an application of the dual Cl-PDED–He-PDPID detector system to analyze a gasoline sample spiked with the EPA 502 mixture. A sample of 5% gasoline in methanol was used for the chromatograms in Fig. 5. Fig. 5b shows a complex chromatogram for the gasoline mixture obtained

from the He-PDPID. On the other hand, in Fig. 5a the Cl-PDED shows almost no response to the injected gasoline sample. After spiking with the EPA 502 mixture in a concentration of 180 ppm, the Cl-PDED selectively responds to those chlorinated compounds spiked in the gasoline matrix, as shown in Fig. 6a. Recoveries for the 15 chlorinated compounds are given in Table 3 and all are over 90%. The response of the Cl-PDED is slightly influenced by the presence of a high concentration of primarily hydrocarbons in the gasoline matrix. The percent response of the Cl-PDED in the presence of a matrix is referred to as the recovery of the response. Since there are too many overlapped peaks in Fig. 6b, it is difficult for the He-PDPID to determine chlorinated compounds in this complex sample under the resolution of the chromatographic column.

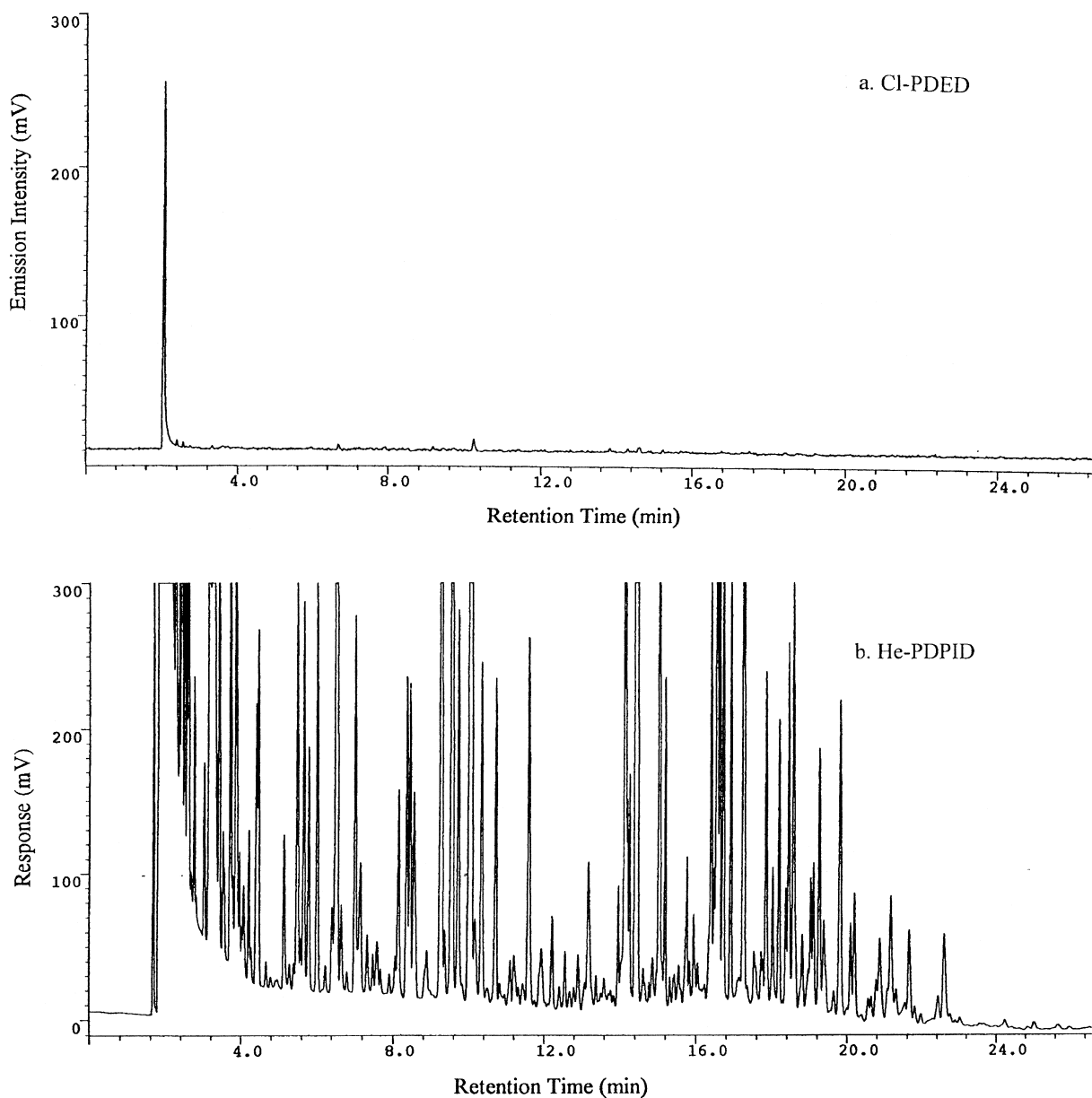


Fig. 5. Chromatograms of gasoline using parallel CI-PDED–He-PDPID detectors. Column: DB-5.625, 30 m \times 0.25 mm I.D., d_f : 0.5 μ m, column exit split ratio (He-PDPID/CI-PDED): 7:1, carrier gas: He, 30 cm/s, oven temperature program: 30°C (5 min), 5°C/min to 70°C, 20°C/min to 130°C (10 min), injector temperature: 200°C, injector split ratio: 100:1, 0.1 μ l 5% gasoline in methanol. (a) CI-PDED. Pulse width: 15 μ s, pulse spacing: 400 μ s, wavelength: 222.1 nm, discharge gas: 0.20% krypton in helium, 3.5 ml/min, detector temperature: 130°C. (b) He-PDPID. Discharge gas: He, 30 ml/min, detector temperature: 200°C.

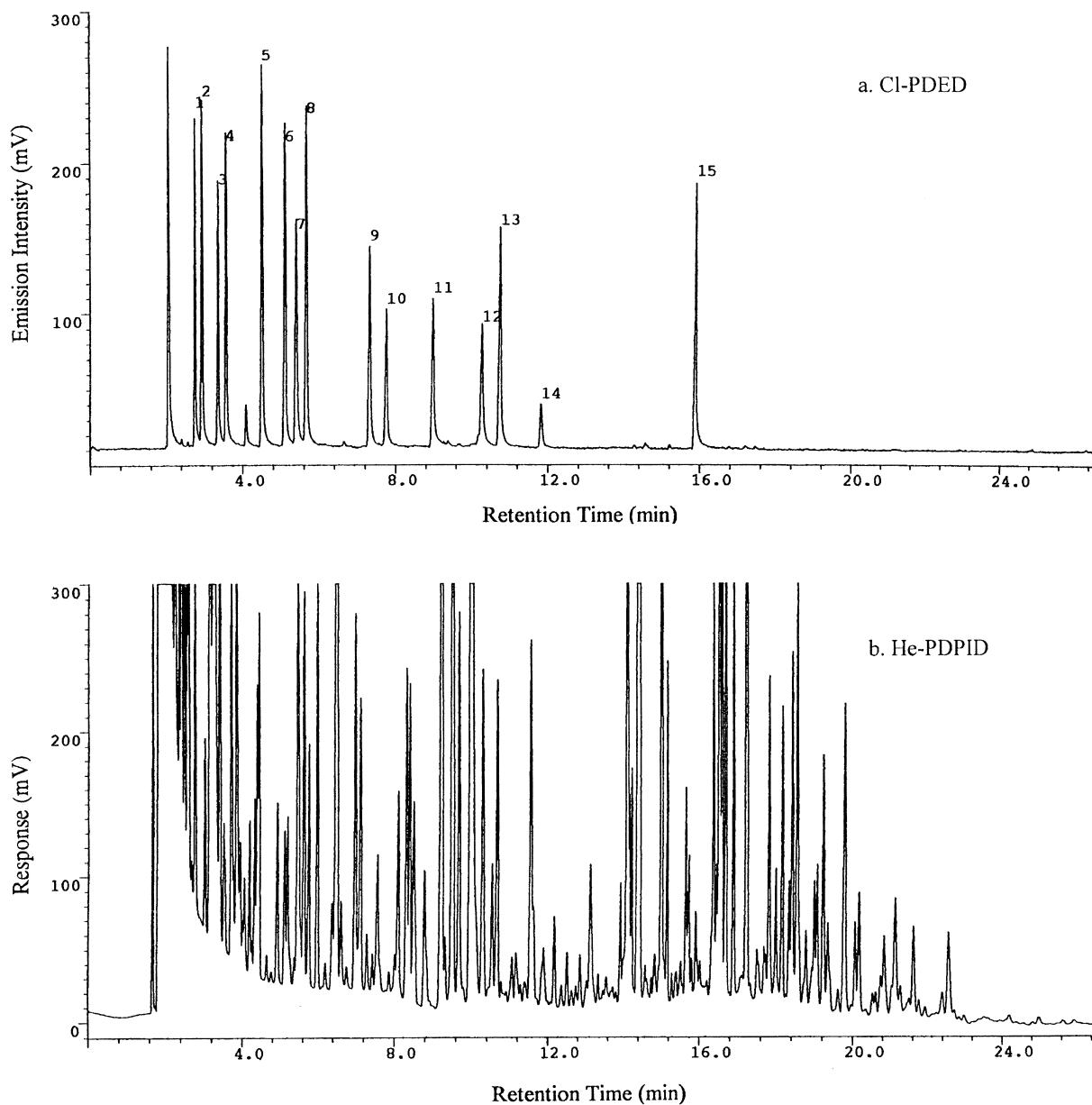


Fig. 6. Chromatograms of matrix spike using parallel CI-PDED–He-PDPID detectors. Column: DB-5.625, 30 m \times 0.25 mm I.D., d_f : 0.5 μ m, column exit split ratio (He-PDPID/CI-PDED): 7:1, carrier gas: He, 30 cm/s, oven temperature program: 30°C (5 min), 5°C/min to 70°C, 20°C/min to 130°C (10 min), injector temperature: 200°C, injector split ratio: 100:1, 0.1 μ l matrix spike (180 ppm each in 5% gasoline matrix). (a) CI-PDED. Pulse width: 15 μ s, pulse spacing: 400 μ s, wavelength: 222.1 nm, discharge gas: 0.20% krypton in helium, 3.5 ml/min, detector temperature: 130°C. (b) He-PDPID. Discharge gas: He, 30 ml/min, detector temperature: 200°C. 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.

Table 3
Recoveries from gasoline matrix

Compounds	Recovery (%)	RSD ^a (%)
1,1-Dichloroethene	92.1	2.4
Methylene chloride	92.3	1.2
<i>trans</i> -1,2-Dichloroethene	92.4	1.7
1,1-Dichloroethane	94.8	1.8
Chloroform	95.3	2.8
1,1,1-Trichloroethane	94.5	3.4
1,2-Dichloroethane	95.6	4.0
Carbon tetrachloride	93.5	2.5
1,2-Dichloropropane	96.1	3.0
Bromodichloromethane	96.1	1.0
<i>cis</i> -1,3-Dichloropropene	90.7	4.1
<i>trans</i> -1,3-Dichloropropene	99.3	2.8
1,1,2-Trichloroethane	93.6	1.5
Dibromochloromethane	97.3	2.9
Tetrachloroethene	95.5	6.1

^a Relative standard deviation from five measurements.

4. Conclusion

The Cl-PDED is a very sensitive chlorine-selective detector for GC, and the He-PDPID is the most sensitive universal detector for GC. The dual Cl-PDED–He-PDPID detector system provides simultaneous determination of chlorinated and non-chlorinated compounds, and the relative response of the two detectors can provide useful qualitative information on peak identification, or evidence for coelu-

tion of a chloro containing compound and a non-chloro containing compound.

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