Short communication

Response factors of organochlorine compounds in the electrolytic conductivity detector

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Abstract

In our previous studies we have used electrolytic conductivity detection (ELCD) in the selective analysis of chlorinated fatty acids in marine samples. In order to determine the chlorinated fatty acids quantitatively, we studied the ELCD response factors (RFs) of chlorinated fatty acids and compared them with those of other chlorinated compounds. We also studied the effect of reactor temperature and total gas flow-rate on the RFs. The ELCD RFs of different organochlorine compounds varied significantly at a reactor temperature of 600°C. The variation was reduced at reactor temperatures higher than 850°C. At low reactor temperatures, the RFs of methyl esters of chlorinated fatty acid were much higher than those of the other compounds. Although the gas flow in the reactor was laminar, diffusion was still rapid enough not to cause the varied RFs. Nitrogen-containing chlorinated compounds had lower RFs than compounds without nitrogen, owing to a neutralization of hydrogen chloride by ammonia. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Electrolytic conductivity detection (ELCD) was first used in gas chromatographic analysis in 1962 [1,2]. Since then it has been developed as an element-selective detection method for compounds containing halogen, nitrogen or sulfur [3–9]. The high selectivity for halogen makes the detector suitable for analysis of organochlorine compounds in complex sample matrices such as environmental samples. For instance, ELCD has been applied to the analysis of chloroanilines and chloronitroanilines in water treatment sledges [10], chlorinated fatty acids in fish and bivalve lipids [11–14] and for the analysis of total organically bound halogen in waste waters [15]. The quantification of such compounds and entities are normally based on the response factor (RF) in ELCD [12,13,16], assuming that unknown compounds have RFs similar to those of reference compounds.

The mechanism of ELCD is not as well studied as those of other detectors for gas chromatography (GC). Diverse results have been reported on the RFs of organochlorine compounds. Ramus and Thomas have studied the reduction of chlorinated hydrocarbons as a function of the nickel reactor tempera-

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ture by connecting a mass spectrometer after an ELCD system [17], varying RFs were found for chlorinated hydrocarbons due to incomplete reduction at reactor temperatures lower than 950°C, the reduction yields varied greatly at 800°C, and the effect depended on the compounds studied. Dolan and co-workers have reported that chlorinated pesticides and polychlorinated biphenyls (PCBs) had dissimilar RFs, which makes it possible to selectively detect chlorinated pesticides in the presence of PCBs by selecting a suitable reactor temperature [6,18]. However, Wu et al. [19] found that the RFs did not change with the chemical structure for compounds that only contained hydrogen, carbon and chlorine when employing a reactor temperature of 820°C. Lopez-Avila and Northcutt [10] also stated that the ELCD response was nearly proportional to the number of chlorine atoms present in the compound, except for some chloroaniline isomers.

Chlorinated fatty acids have been found in fishes and bivalves in our previous studies [11–14]. As the dechlorination of chlorinated fatty acid methyl esters (FAMEs) has not been studied previously, the objective of the present study was to compare the RFs of chlorinated FAMEs with those of other chlorinated compounds already studied by GC–ELCD, and to evaluate experimental parameters that might influence the RFs. The effects of the reactor temperature, the total gas flow in the reactor, and the concentration of chlorinated compounds were studied.

2. Experimental

2.1. Chemicals

The chemicals used were of reagent or analytical-reagent grade. A homologous series of monochlorinated FAMEs and a homologous series of dichlorinated FAMEs were synthesized by J. Skramstad and P. Frøyen (Oslo University, Norway) from the corresponding monoenoic analogues (methyl hexadecenoate to methyl tetracosenoate, from Larodan Fine Chemicals, Malmö, Sweden) using the methods presented by Lyness and Quackenbush [20] and Frøyen and Skramstad [21].

Stock solutions of the organochlorine compounds were prepared by dissolving them in cyclohexane,

and they were further diluted by cyclohexane to about 5 ng/μl chlorine. 1-Chlorooctadecane was used as the internal standard.

2.2. Gas chromatography

A Varian GC system Model 3700 with Autosampler series 8000, used in the splitless injection mode, was equipped with a polar column (DB23, 30 m×0.53 mm I.D., film thickness=0.5 μm, J&W, USA). Helium (99.9996%; Air Liquide, Sweden) was used as the carrier gas (8 ml min^{-1}) and make-up gas. A glass splitter divided the GC effluent to two detectors, a flame ionization detection (FID) system and an ELCD system (Tracor/Varian, Model 1000). The detector signals (peak area) were recorded on Hewlett-Packard Model 3390A reporting integrators.

The initial oven temperature, 60°C, was held for 3 min and then programmed at a rate of 4°C min^{-1} to a final temperature 230°C. The injector temperature was 260°C. The FID system was operated at 300°C. The ELCD system reactor temperature was varied from 250 to 950°C and the base temperature was 280°C.

2.3. Electrolytic conductivity detector

The ELCD system was operated in the reductive mode, and hydrogen (99.9997%; AGA, Sweden) was used as reaction gas. The reaction tube length was 84 mm and the inner diameter was 0.8 mm. A small-volume cylinder cell was utilized for mixing, separating, and monitoring the concentration of conducting species. 1-Propanol, recirculated through an ion-exchanger, was employed as the conductivity solvent at a flow-rate of 0.50 ml min^{-1}.

The effect of the reactor temperature was studied under constant gas flow on injecting equal amounts of chlorinated compounds. The effect of the total gas flow was studied by changing make-up gas and reaction gas; the carrier gas flow was kept constant (10 ml min^{-1}) as well as the mole fraction of hydrogen and helium ($X_{H2} = X_{He} = 0.5$). The column was only connected to the ELCD system during the study of gas flow in order to prevent an altered split ratio between the ELCD and the FID systems on varying the gas flows in the ELCD system.

2.4. Calculations

2.4.1. Reynolds number (Re)

The Re was calculated according to Coulson and Richardson [22]

$$Re = ud\rho/\mu \tag{1}$$

where u is velocity, d is inner diameter of the reaction tube (0.8 mm), ρ is the gas density (0.025 kg m^{-3} at 850°C) and μ is the gas viscosity (174· 10^{-7} kg s^{-1} m at 850°C, calculated according to Reid et al. [23]).

2.4.2. Diffusion coefficients

In the binary mixture of hydrogen and helium, the diffusion coefficient of the gas mixture was calculated accordingly [22,24]

$$D_{ij} = 10^{-3}T^{1.75}[(M_i + M_j)/(M_iM_j)]^{0.5}/\{P\,[(\textstyle\sum v)_i^{0.33} + (\textstyle\sum v)_j^{0.33}]^2\} \tag{2}$$

D_{ij} is the diffusion coefficient of hydrogen and helium (cm^2/s) and expresses the diffusion of both components; T is the absolute temperature; M_i and M_j are the molecular masses of hydrogen and helium; P is the pressure in atmospheres; and v is the atomic diffusion volume [22,24].

The diffusion coefficients of the chlorinated compounds in the gas mixture of hydrogen and helium was calculated according to Blanc's law

$$D_{im} = [\textstyle\sum(x_j/D_{ij})]^{-1} \tag{3}$$

which is useful for the case of a trace species diffusing through a multi-component mixture

Table 1
Response factor (RF, area units g^{-1} Cl) of organochlorine compounds in ELCD at 900°C[a]

Organochlorine compound	RF·10^{-13}	S_{rel} (%)	Relative RF	Correlated relative RF
Benzyl chloride	7.0	4.9	1.0	0.9
Hexachlorobenzene	8.6	6.1	1.2	0.9
Lindane	13.4	0.5	1.9	1.3
2-Chloronitrobenzene	5.2	5.2	0.8	0.7
2-Chloroaniline	5.2	3.1	0.7	0.7
3-Chloroaniline	5.6	5.5	0.8	0.7
4-Chloroaniline	4.8	5.8	0.7	0.7
1-Chlorodecane	8.0	4.4	1.1	0.9
1-Chlorododecane	7.4	6.3	1.1	0.9
1-Chlorotetradecane	7.4	1.8	1.0	0.9
1-Chlorohexadecane	7.2	2.6	1.0	1.0
1-Chlorooctadecane	7.0	2.5	1.0	1.0
Methyl 9(10)-monochlorohexadecanoate	5.8	6.1	0.8	1.0
Methyl 9(10)-monochlorooctadecanoate	5.8	4.5	0.8	1.0
Methyl 11(12)-monochloroeicosanoate	5.6	5.7	0.8	1.0
Methyl 13(14)-monochlorodocosanoate	5.0	4.7	0.7	1.0
Methyl 15(16)-monochlorotetracosanoate	4.2	2.4	0.6	1.0
Methyl 9,10-dichlorohexadecanoate	5.6	6.7	0.8	1.1
Methyl 9,10-dichlorooctadecanoate	4.4	3.0	0.6	1.0
Methyl 11,12-dichloroeicosanoate	3.6	2.4	0.5	0.9
Methyl 13,14-dichlorodocosanoate	3.0	4.2	0.4	0.9
Methyl 15,16-dichlorotetracosanoate	2.6	3.2	0.4	0.9

[a] S_{rel} is the relative standard deviation (%) of RF for $n=6$. The relative RF=RF of organochlorine compound/RF of 1-chlorooctadecane (internal standard). The correlated relative RF=[(relative RF of ELCD/relative RF of FID)·(N/18)], where N is the carbon number in the compound.

[25,26]. $D_{i\text{m}}$ is the diffusion coefficient of a chlorinated compound (i) in a gas mixture (m), in this case a ternary system; x_j are mole fractions of hydrogen ($x_j = 0.86$) and helium ($x_j = 0.14$); D_{ij} is the diffusion coefficient of a chlorinated compound in a binary system as calculated from Eq. (2), where the chlorinated compound (i) is one of the components and hydrogen (j) or helium (j) is the other. The calculated diffusion coefficients are given in Table 2.

2.4.3. Transfer time

The time (t) demanded for a chlorinated compound to reach the catalyst surface was estimated from the diffusion coefficient according to Ref. [27]

$$x = (2Dt)^{0.5} \tag{4}$$

where x is the root mean square distance covered when particles diffuse in one dimension during time t.

3. Results and discussion

3.1. Effect of reactor temperature on response factors

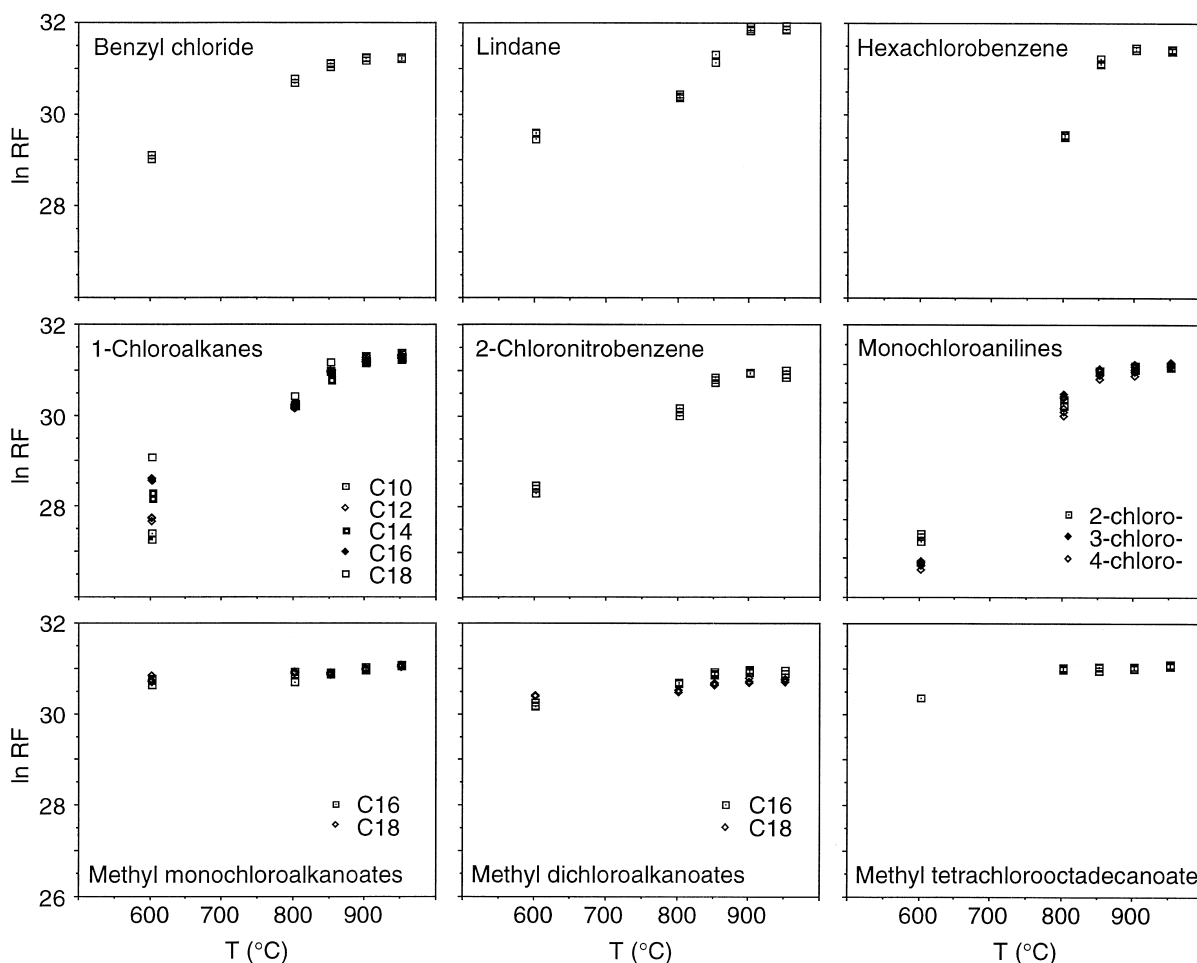The RF was defined as the peak area per mass of injected chlorine (Cl), and was found to vary sig-

Fig. 1. The effect of reactor temperature on the response factors of organochlorine compounds. Reaction gas flow was 50 ml min^{-1}, solvent 0.5 ml min^{-1}, carrier gas flow 8 ml min^{-1}. A 2-μl solution sample was injected on the DB23 column.

nificantly for several of the organochlorine compounds (Table 1). When expressed as a relative RF, with 1-chlorooctadecane as the internal standard, the values ranged from 0.4 to 1.9. The variation can be a combined result of the contributions from different parts of the GC system. To eliminate the variation caused by possible adsorption losses on the column, the ELCD responses were correlated with the corresponding FID responses. The correlated relative RFs ranged from 0.7 to 1.3, indicating that column adsorption did affect the ELCD response. For the three homologous series of monochloroalkanes, monochlorinated and dichlorinated FAMEs, the FID-correlated relative RFs ranged from 0.9 to 1.1, indicating that the homologues had quite similar RFs in the ELCD system.

The RFs of most of the compounds increased significantly in the temperature range 600 to 850°C (Fig. 1). Above this range the temperature dependency disappeared with a tendency for a maximum RF at 900°C. This confirms the general advice given for ELCD to use a reactor temperature of 850°C [28]. No ELCD response was obtained for hexachlorobenzene at 600°C. The supplied energy at the low reactor temperature was probably not sufficient to break its C–Cl bond, because aromatic C–Cl bonds have a bond dissociation energy of 4–13 kcal mol^{-1} larger than aliphatic C–Cl bonds [6] (1 cal=4.184 J).

The variation of the RFs of the monochlorinated, dichlorinated and tetrachlorinated FAMEs was rather small and these compounds typically gave much higher RFs than the other compounds at the lower temperatures. Extended studies on the chlorinated FAMEs at reactor temperatures below 600°C (Fig. 2) showed that the RFs were rather constant down to 500°C and that the chlorinated FAMEs already gave responses at 250°C.

3.2. Effect of total gas flow in the reactor on response factors

The total gas flow through the detector was varied between 20 and 120 ml min^{-1} in a study of its effect on the RFs. The mole fraction of hydrogen in the reactor was kept constant to prevent any effect on the RFs by a change in the hydrogen concentration. The study was conducted with lindane, 2-chloronit-
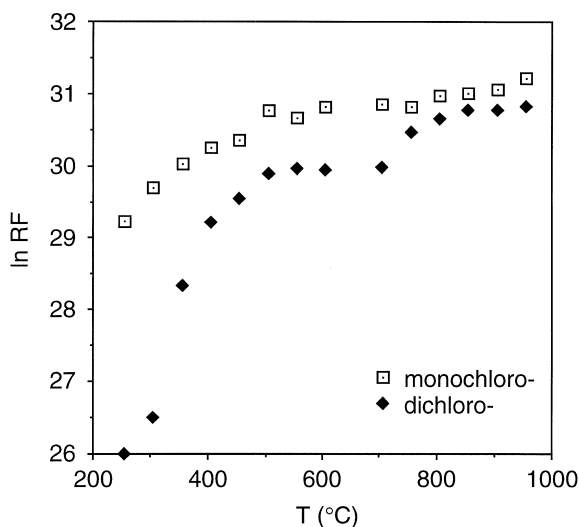

Fig. 2. The effect of reactor temperature on the response factors (mean values, $n=3$) of methyl monochloro- and dichlorooctadecanoate. Reaction gas flow was 50 ml min^{-1}, solvent 0.5 ml min^{-1}, carrier gas flow 8 ml min^{-1}. A 1-μl solution sample was injected on the DB23 column.

robenzene, 1-chlorooctadecane, hexachlorobenzene and a homologous series of dichlorinated FAMEs (methyl dichlorohexadecanoate to methyl dichlorotetracosanoate). For the first four compounds the RFs decreased with increased total gas flow through the reactor (Fig. 3), suggesting that the higher gas flow should be avoided. Similar results were obtained under different reactor temperatures (Fig. 3). The low ELCD response at a high gas flow is difficult to explain especially in view of the complexity of the detection system. It may be caused by the short residence time of the compounds in the reactor, leading to incomplete dechlorination. However, this is difficult to prove, because other possibilities also existed, such as a reduced temperature of the Ni reactor due to the high gas flow.

3.3. Detector linearity

The linearity of the ELCD response was tested for methyl 9,10-dichlorooctadecanoate, which has been found in fish samples [11,12]. The range tested was from 1 to 1000 ng Cl/μl at 850°C, using 50 ml min^{-1} reaction gas flow. A good linearity was observed between 1 to 500 ng Cl/μl (correlation
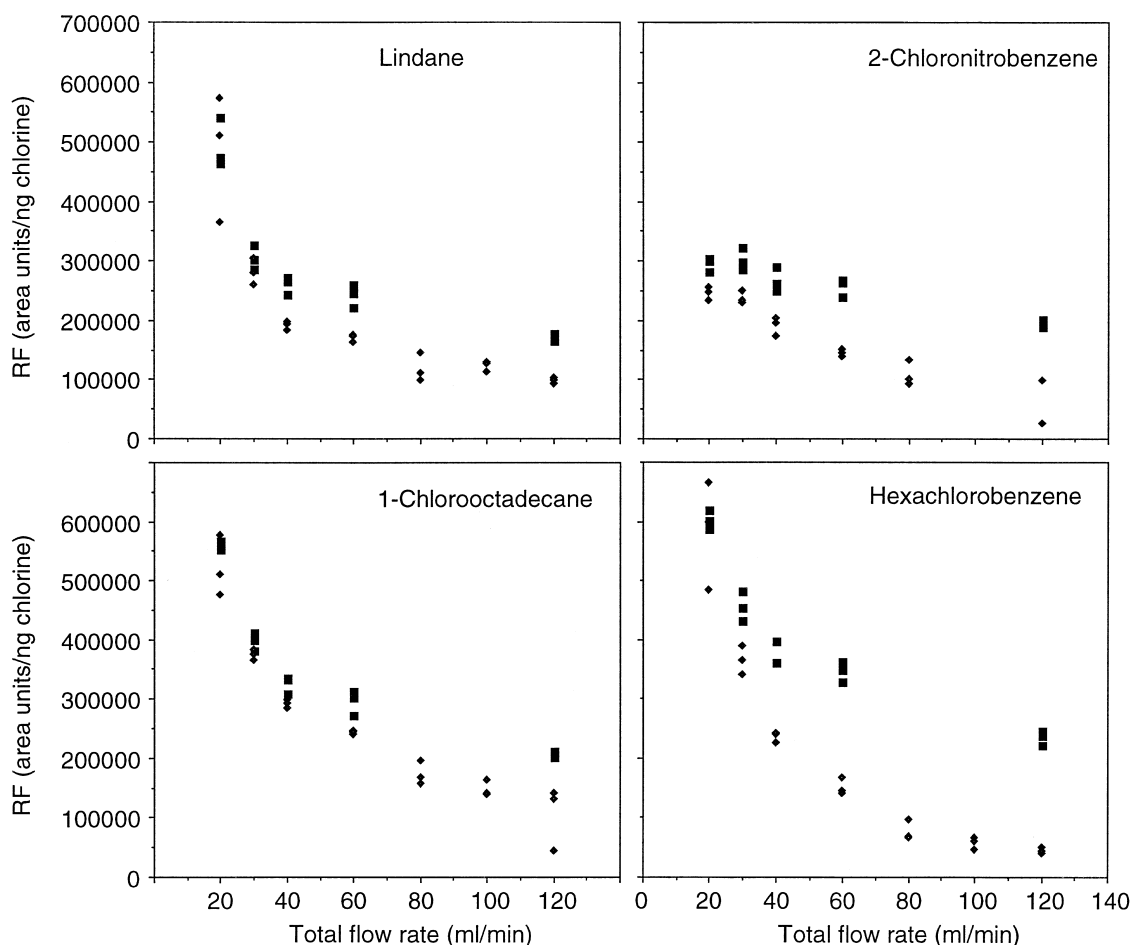
Fig. 3. The relation between the response factors of organochlorine compounds and the total gas flow-rate in the reactor. Mole fractions of hydrogen and helium were 0.5, carrier gas flow was 10 ml min^{-1} and solvent flow-rate was 0.5 ml min^{-1}. A 1-μl solution sample was injected on the DB23 column. ($\blacklozenge$) Represents 850°C and ($\blacksquare$) represents 950°C.

coefficient 0.999). Methyl dichlorooctadecanoate and several of the other chlorinated compounds in Table 1 were studied in the range of 1 to 10 ng Cl/μl, and they produced linear responses with correlation coefficients of 0.99.

3.4. The diffusion coefficient of organochlorine compounds

The mixing between the reaction gas (H_2) and the organochlorine compounds, and their transport rates to the catalytic surface are processes that may affect the completeness of the dechlorination reaction. Both

processes depend on convection and diffusion. Thus, the flow pattern and the diffusion of the reactants inside the reactor were estimated.

The reaction gas enters the reaction tube perpendicular to the carrier gas coming from the GC column. This would result in a well-mixed gas mixture at the entrance of the reaction tube. In the determination of the RFs, the total mean gas velocity in the reaction tube (after the mixing point) was 7.25 m s^{-1} (850°C), which corresponds to a Reynolds number of 8. This indicates a laminar flow since a Reynolds number less than 2000 corresponds to laminar flow [22]. The laminar flow pattern in the

reaction tube may make diffusion transport of the reactants (hydrogen and chlorinated compounds) to be an important parameter for the RFs.

The time (t) demanded for a chlorinated compound to reach the catalyst surface by diffusion was calculated by substituting the radius of the reaction tube (0.4 mm) for x in Eq. (4). We found that the necessary diffusion time ranged between 0.4–0.8 ms at 600°C and 0.2–0.5 ms at 950°C for the whole range of compounds in Table 2. These values are much smaller than the residence time in the reactor (10–14 ms at a reactor temperature of 600–950°C). This implies that the chlorinated compounds will be efficiently transported by diffusion to the catalyst surface during their residence time in the reactor and diffusion transport would therefore not limit the RFs.

3.5. The influence of nitrogen in organochlorine compounds on their RFs

A comparison between organochlorine compounds only comprising carbon, hydrogen and chlorine and organochlorine compounds also containing nitrogen showed that the latter ones had relatively low response factors (Table 1). Lopez-Avila and Northcutt [10], who studied chloroanilines and chloronitroanilines with GC–ELCD, also reported similar results. According to the Kohlrausch's law of independent migration of ions, the contribution of an ion to the equivalent conductance of electrolytes (Λ_0) appears to be constant and independent of the other ions present [29]. The equivalent conductance at 25°C of the separate ions (λ_0) for hydrogen ion, ammonium and chloride are 350, 74 and 76 (ohm^{-1} cm^{-1} l.equiv.$^{-1}$), respectively [30]. Ammonium chloride has a lower conductivity [$\Lambda_0(NH_4Cl) = \lambda_0(NH_4^+) + \lambda_0(Cl^-) = 150$] than hydrogen chloride [$\Lambda_0(HCl) = \lambda_0(H^+) + \lambda_0(Cl^-) = 426$]. Thus, lower RFs for nitrogen containing compounds might be caused by the contemporary formation of ammonia, which neutralizes hydrogen chloride and leads to the formation of ammonium chloride.

Table 2
Diffusion coefficients of organochlorine compounds in a mixture of hydrogen and helium estimated from Eq. (3)[a]

Compound	Diffusion coefficient (cm^2 s^{-1})				
	600°C	800°C	850°C	900°C	950°C
Benzyl chloride	1.91	2.75	2.97	3.21	3.45
Hexachlorobenzene	1.58	2.27	2.46	2.65	2.86
Lindane	1.54	2.21	2.39	2.58	2.78
2-Chloronitrobenzene	1.95	2.80	3.03	3.27	3.51
2-Chloroaniline	2.00	2.87	3.11	3.35	3.61
3-Chloroaniline	2.00	2.87	3.11	3.35	3.61
4-Chloroaniline	2.00	2.87	3.11	3.35	3.61
1-Chlorodecane	1.55	2.23	2.41	2.60	2.80
1-Chlorododecane	1.42	2.04	2.21	2.39	2.57
1-Chlorotetradecane	1.32	1.90	2.05	2.22	2.38
1-Chlorohexadecane	1.24	1.78	1.92	2.08	2.23
1-Chlorooctadecane	1.17	1.68	1.81	1.96	2.11
Methyl 9(10)-monochlorohexadecanoate	1.19	1.71	1.85	1.99	2.15
Methyl 9(10)-monochlorooctadecanoate	1.13	1.62	1.75	1.89	2.03
Methyl 11(12)-monochloroeicosanoate	1.07	1.54	1.66	1.80	1.93
Methyl 13(14)-monochlorodocosanoate	1.02	1.47	1.59	1.72	1.85
Methyl 15(16)-monochlorotetracosanoate	0.98	1.41	1.52	1.64	1.77
Methyl 9,10-dichlorohexadecanoate	1.16	1.67	1.80	1.95	2.09
Methyl 9,10-dichlorooctadecanoate	1.10	1.58	1.71	1.85	1.99
Methyl 11,12-dichloroeicosanoate	1.05	1.51	1.63	1.76	1.89
Methyl 13,14-dichlorodocosanoate	1.00	1.44	1.56	1.68	1.81
Methyl 15,16-dichlorotetracosanoate	0.96	1.38	1.50	1.62	1.74

[a] The mole fractions of hydrogen and helium were $X_{H2} = 0.86$ and $X_{He} = 0.14$; pressure was 1 atm; diffusion volume $(\Sigma v)_{H2} = 7.1$, $(\Sigma v)_{He} = 2.9$, and $(\Sigma v)_{RCl}$ ranged from 136 to 558 (1 atm = 101 325 Pa).

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