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# Experimental determination of chlorine isotope separation factor by anion-exchange chromatography

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Received 10 July 2003; received in revised form 18 November 2003; accepted 18 November 2003

## Abstract

Chlorine isotope fractionation factor was determined by strongly basic anion-exchange chromatography with 0.1 mol/l HCl at 25 °C. The magnitude of the factor was calculated as a single-stage separation factor of 1.00030 with analytical precision of 0.00006 (1 $\sigma$ ). The results showed that the lighter isotope (<sup>35</sup>Cl) was preferentially fractionated into the resin phase, while the heavier one (<sup>37</sup>Cl) enriched into the aqueous phase. This trend suggested that the hydrated Cl<sup>−</sup> ions in the aqueous phase were slightly more stable than the hydrated Cl<sup>−</sup> ions electrostatically interacting with the ion-exchange groups of the resin.

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**Keywords:** Chlorine; Isotope; Separation factor; Anion-exchange; Chromatography

## 1. Introduction

Chlorinated organic compounds (COCs) are known as serious pollutants. Since they are not readily decomposed in nature, their existence in atmosphere, aquifer, and lithosphere is an acute problem relating to the global warming and environmental pollution. To trace their source, behavior and natural fate is a major concern in controlling pollutants for the environment protection.

A study using stable chlorine isotopes (<sup>37</sup>Cl and <sup>35</sup>Cl) has shown the significant difference in  $\delta^{37}\text{Cl}$  (versus standard mean ocean chloride: SMOC/‰) between naturally occurring Cl-bearing substances and man-made chlorinated compounds [1]. The  $\delta^{37}\text{Cl}$  values of the several man-made COCs varied from −6.80 to +2.61‰, while those of the natural materials ranged within 2‰. It was explained that this large

fractionation obtained for man-made COCs occurred during the manufacturing processes. If this is the case, the  $\delta^{37}\text{Cl}$  value could be useful to identify the source of the Cl-bearing compounds.

Van Warmerdam et al. [2] studied several chloro-carbon compounds and measured their  $\delta^{37}\text{Cl}$  values and carbon isotope ratios (in notation of  $\delta^{13}\text{C}/\text{‰}$ ). Based on the C–Cl isotope diagram, they systematized COCs such as PCE, TCE, and TCA. Recently, Jendzejewski et al. [3] applied the C–Cl isotopic combination to the characterization of the chlorinated hydrocarbons. The C–Cl diagram could thus be a potential index for fingerprints of the COCs and a monitoring tool for the transport process and natural fate of COCs in air and ground water.

Compared with the carbon isotope geochemistry, chlorine isotope effects are not well established yet. However, if understood well, the Cl isotope geochemistry would become an effective tool for the investigation on the biodegradation and reductive dehalogenation of the COC pollutants [4]. For this reason, it is necessary to know chlorine isotope separation factors between two phases and/or two chemical species involving Cl. There are several experimental reports on measurements of Cl isotope fractionation based on kinetic isotope effects such as chemical diffusion [5]. However, no reliable measurement of the equilibrium Cl isotope

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effects has so far been reported. In this study, we performed a chromatographic experiment on Cl isotopes by using a 30 cm anion-exchange column. The separation factor was estimated and discussed from the viewpoint of the isotope distribution theory [6] and hydration effect.

## 2. Experimental

In order to determine the chlorine isotope separation factors, the anion-exchange chromatography in the band displacement manner was performed at Sophia University. A single operation yielded two results of the Cl isotope separation factor: one from front part of the band and the other from the rear part. This study employed a chromatographic column made of Pyrex glass with a water jacket. The column was 30 cm  $\times$  1 cm i.d. Temperature of the column was kept constant at  $25.0 \pm 0.2$  °C throughout the experiment by passing temperature-controlled water through the water jacket. The study used a strongly basic anion exchanger, Muromac 1  $\times$  8 analytical grade (mesh size, 200–400 mesh; ionic form,  $\text{Cl}^-$ ; total exchange capacity, 1.2 eq./l; cross linkage, 8% divinylbenzene (DVB); moisture, 45–55%). The resin was packed in the column and was conditioned to the hydroxide form with 2 mol/l NaOH fed into the column by a high pressure pump (Nihon Seimitsu). Then, Cl-free distilled water was fed into the column in order to flash sodium ions out of the column. The resin bed height in the column was 30 cm and its volume was calculated at 24 ml.

The standard Cl solution, 0.1 mol/l HCl, was first fed from top of the column with a constant flow rate to form a Cl adsorption band. The  $\text{Cl}^-$  band was then eluted with an eluent of 0.1 mol/l  $\text{HNO}_3$ ; the ion exchanger showed the higher selectivity to the nitrate ion than the chloride ion, and hence nitrate ions replaced chloride ions. The flow rate was kept constant by the high pressure pump throughout an experiment. The effluent from the bottom of the column was automatically collected and divided into small fractions by a fraction collector. The volume of a fraction was 8.0 ml.

The  $\text{Cl}^-$  ion concentration in each fraction of the effluent was measured by absorption spectroscopy. Chloride ions in an aliquot of the selected fractions were extracted as AgCl by adding  $\text{AgNO}_3$  solution. The precipitant was subsequently converted to  $\text{CH}_3\text{Cl}$  by a reaction with  $\text{CH}_3\text{I}$ . The  $\text{CH}_3\text{Cl}$  thus obtained was purified by gas chromatography, and submitted into a mass spectrometer. The Cl isotope ratio ( $\delta^{37}\text{Cl}$  versus SMOC) of the  $\text{CH}_3\text{Cl}$  was measured on a VG SIRA 24 mass spectrometer at the Utrecht University with a precision of 0.06‰ (1 $\sigma$ ) [7].

## 3. Results and discussion

Experimental results are summarized in Table 1. The  $\text{Cl}^-$  ion was free in the first 212 ml of the effluent. Its concentration then jumped up to 0.10 mol/l and was nearly constant

Table 1

Analytical results on Cl isotope composition and  $\text{Cl}^-$  ion concentration of the experiment with a short column

	Volume (ml)	Cl (mol/l)	$\delta^{37}\text{Cl}$ (‰)	$^{35}\text{Cl}$ molar fraction	$\varepsilon^a$
	0	0.000			
	⋮	⋮			
	212	0.000			
Front	220	0.110	0.563	0.77324	
	228	0.103	0.361	0.77339	
	236	0.100	0.274	0.77345	
	244	0.101	0.160	0.77353	
	252	0.101	0.107	0.77357	
	260	0.102	0.038	0.77362	
	300	0.105	0.001	0.77365	0.00024
	340	0.102	0.010	0.77364	
	380	0.106	0.026	0.77363	
	420	0.104	0.003	0.77365	
	460	0.108	−0.019	0.77366	
	500	0.103	0.012	0.77364	
	540	0.111	−0.031	0.77367	
	580	0.109	0.015	0.77364	
Rear	588	0.108	0.003	0.77365	
	596	0.109	−0.045	0.77368	
	604	0.107	−0.278	0.77385	
	612	0.100	−0.771	0.77421	
	620	0.101	−1.111	0.77445	0.00035
	628	0.000			
	⋮	⋮			
	660	0.000			

<sup>a</sup> These values were separately obtained from both the front part and the rear part of the band (see text).

at 0.110 mol/l between 220 and 620 ml of the effluent. The  $\text{Cl}^-$  ion concentration reflected that of the  $\text{HNO}_3$  in the eluent because chromatography was operated in the band displacement manner. After 620 ml of the effluent passed, the  $\text{Cl}^-$  ion concentration fell to 0 mol/l and remained to be the value, hereafter. The  $\text{Cl}^-$  ion concentration profile indicates that the band displacement chromatography was carried out ideally. The chromatogram and  $^{35}\text{Cl}$  isotopic molar fractions of this experiment are shown in Fig. 1. From left to right in the figure, the  $^{35}\text{Cl}$  molar fraction curve quickly increased from the lowest value of 0.77324 to the original value of 0.77365. After being steady, it again steeply increased up to the highest value of 0.77445, which corresponds to a 1.0‰ enrichment in the rear-most fraction compared with that of the original. The  $^{37}\text{Cl}$  molar fraction profile indicated that the lighter isotope depleted in the front part and enriched in the rear part of the chromatogram, meaning that  $^{35}\text{Cl}$  was preferentially fractionated into the ion-exchanger phase and  $^{37}\text{Cl}$  was into solution phase.

### 3.1. Single-stage separation factor

In order to evaluate the magnitude of the Cl isotope effect observed in the present experiment, the single-stage separation factor expressed as  $S (= \varepsilon + 1)$  for the  $^{37}\text{Cl}/^{35}\text{Cl}$  isotopic

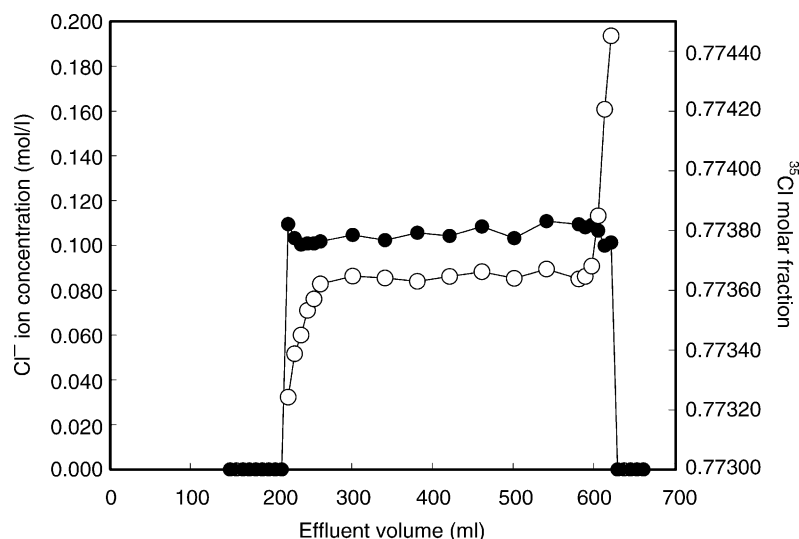


Fig. 1. The  $^{35}\text{Cl}$  molar fraction and  $\text{Cl}^-$  ion concentration profiles of the experiment with the 30 cm anion-exchange column. The line connecting solid circles shows the  $\text{Cl}^-$  concentration profile (left vertical axis for the scale), and the curve connecting open circles represents the  $^{35}\text{Cl}$  isotopic molar fractions (right vertical axis for the scale). The  $^{35}\text{Cl}$  isotopic molar fraction in the feed solution is 0.77365.

pair was calculated. The  $S$  is defined as

$$S = \left( \frac{[\text{Cl}^{37}]/[\text{Cl}^{35}]}{[\text{Cl}^{37}]/[\text{Cl}^{35}]} \right) \quad (1)$$

where  $[A]$  and  $[\bar{A}]$  denote the concentrations of isotope  $A$  in the solution phase and in the ion-exchanger phase, respectively. The  $\varepsilon$  is calculable by using the following equation defined by [8]

$$\varepsilon = \sum \left[ \frac{|R_i - R_0|w_i}{R_0(1 - R_0)Q} \right] \quad (2)$$

where  $R_0$  is the  $^{35}\text{Cl}$  isotopic molar fraction in the feed solution,  $R_i$  that in the  $i$ th fraction of the effluent,  $w_i$  the amount of the chloride ion in the  $i$ th fraction and  $Q$  is the total exchange capacity of the exchanger for chloride. In this study, the  $Q$  value was calculated at 0.02139 mol. The summation is taken over all the fractions that are enriched or depleted in  $^{35}\text{Cl}$ .

By using Eq. (2) and the analytical results, the  $\varepsilon$  values were calculated as  $2.4 \times 10^{-4}$  for the front part (220–300 ml) and  $3.5 \times 10^{-4}$  for the rear part (580–620 ml) of the experiment (Table 1). The average of two  $\varepsilon$  values was  $3.0 \times 10^{-4}$ , giving the  $\text{Cl}$  fractionation factor of 1.00030 at  $25.0^\circ\text{C}$ . This value shows that the heavier isotope enriched into solution phase in the present system. The factor implied that  $\text{Cl}$  isotope fractionation between  $\text{Cl}$  in anion exchanger and  $\text{Cl}$  in solution may cause 0.3‰ enrichment of  $\delta^{37}\text{Cl}$  into the solution at  $25^\circ\text{C}$ .

### 3.2. Chlorine isotope effect based on an isotope two-phase distribution theory [6]

The theory on isotope distribution between two phases [6] correlates  $S$  with the isotopic reduced partition function

ratios (RPFRs) defined by Bigeleisen and Mayer [9] and the molar fractions of the chemical species containing the isotopes in concern in the separation system. Based on the theory, the  $S$  is in general expressed as

$$\ln S = \ln \left( \sum x_i f_i \right) - \ln \left( \sum \bar{x}_i \bar{f}_i \right) \quad (3)$$

where  $x_i$  and  $f_i$  are the molar fraction and the RPFR of species  $i$  in the solution phase, respectively. The  $\bar{x}_i$  and  $\bar{f}_i$  are the corresponding quantities in the resin phase.  $\sum x_i = \sum \bar{x}_i = 1$ . Symmetry numbers are neglected in the expressions of the RPFRs for simplicity.

### 3.3. Hydration

The only viable chlorine species in the solution and ion-exchanger phase of the present experiment is the hydrated chloride ion. We denote them as  $\text{Cl}^-(\text{H}_2\text{O})_n$  and  $\text{Cl}^-(\text{H}_2\text{O})_m$ , where  $n$  and  $m$  are the hydration numbers in the former phase and in the latter phase, respectively. In this case, Eq. (3) is simplified to

$$\ln S = \ln f_n - \ln \bar{f}_m \quad (4)$$

where  $f_n$  is the  $^{37}\text{Cl}$ -to- $^{35}\text{Cl}$  isotopic RPFR of  $\text{Cl}^-(\text{H}_2\text{O})_n$  in the solution phase while  $\bar{f}_m$  is that of  $\text{Cl}^-(\text{H}_2\text{O})_m$  in the ion-exchanger phase.

Eq. (4) may be rewritten as

$$\ln S = \ln(f_n/f_m) - \ln(\bar{f}_m/f_m) = \ln S_{\text{hydration}} - \ln S_{\text{phase}} \quad (5)$$

By definition,  $S_{\text{hydration}}$  can be regarded as the separation factor that originates from a change in the hydration number from  $m$  to  $n$  in the solution phase. The value of  $n$  is normally larger than that of  $m$  [10], and therefore, value of  $\ln S_{\text{hydration}}$  is expected to be positive. By definition, the  $S_{\text{phase}}$  is the separation factor observed when the simple hydrated species,

$\text{Cl}^-(\text{H}_2\text{O})_m$ , is transferred from the ion-exchanger phase to the solution phase. The value of  $\ln S_{\text{phase}}$  may be positive because the RPFR of the hydrated  $\text{Cl}^-$  ions further surrounded by water molecules in the second and higher-order hydration spheres with the interaction with the ion-exchange groups of the ion exchanger is expected to be slightly larger than that of hydrated  $\text{Cl}^-$  ions simply surrounded by water molecules in the second and higher-order hydration spheres without the interaction. The present experimental results support the relation as  $\ln S_{\text{hydration}} > \ln S_{\text{phase}}$ .

For the isotope effect in this resin system, only the electrostatic interaction is responsible, because the resin used is strongly basic one ( $-\text{NR}_4^+$ ). It is thus reasonable to consider that anions are simply hydrated rather than form ion-pairs in the resin phase, as they are in the solution phase, although there are neither papers on hydrated anions nor spectroscopic evidence on the hydration mode of  $\text{Cl}^-$  anions in literature. We suppose that the electrostatic interaction may occur outside the primary hydration sphere. To prove it, we are currently performing the molecular orbital (MO) calculations on the  $\text{Cl}^-$  species modeling  $\text{Cl}^-$  ions in the solution phase and in the resin phase of ion-exchange systems. We hope that MO results will compute the RPFR and hydration numbers of those hydrated species and figure the circumstances of the  $\text{Cl}^-$  ions in both the solution and the resin phases. We will be able to report the results in future papers.

#### 4. Conclusions

The major findings of this experimental study on  $\text{Cl}^-$  isotope separation by anion-exchange chromatography are summarized below.

- (1) The  $\text{Cl}^-$  isotope separation was realized by strongly basic anion-exchange chromatography with 0.1 mol/l  $\text{HCl}$  operated in the band displacement manner.
- (2) The  $\text{Cl}^-$  isotope fractionation factor was calculated as a single-stage separation factor of 1.00030 at 25.0 °C with precision of 0.00006 ( $1\sigma$ ).
- (3) The heavier isotope,  $^{37}\text{Cl}$ , was preferentially fractionated into the aqueous phase, while the lighter isotope,  $^{35}\text{Cl}$ , was enriched into the resin phase.
- (4) The magnitude and sign of the separation factor suggest that the isotope effect accompanying hydration is larger than the isotope effect due to the phase change in this experimental system.

#### Acknowledgements

We gratefully appreciate Mr. Arnold van Dijk for the mass-analytical assistance. This study was financially supported by a grant-in-aid from the Japan Society for Promotion of Science (No. 801-12680526).

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