Use of carbon stable isotope to investigate chloromethane formation in the electrolytic dechlorination of trichloroethylene

Yuanxiang Fang, Souhail R. Al-Abed *

National Risk Management Research Laboratory, USEPA 26 W. Martin Luther King Dr. Cincinnati, OH 45268, United States

Abstract

Carbon stable isotope trichloroethylene (^{13}C TCE) was used to investigate the formation of chloromethane (CM) during the electrolytic dechlorination of trichloroethylene (TCE) at a granular-graphite packed cathode. A method was developed to use a conventional GC/MS to analyze and quantify regular and ^{13}C TCE and their dechlorination products. The concentration of a ^{13}C compound can be calculated, based on the concentration of its regular counterpart, from the response ratio of two fragments of different mass per charge values from the compounds in a sample and two characteristic MS spectrum ratios: one is the response ratio of the two fragments of the regular compound, and the other is the response ratio of the corresponding fragments of the regular and ^{13}C compounds at the same concentrations. The method was used to analyze the regular and ^{13}C compounds observed in an experiment of dechlorination in an ammonium acetate solution that contained both regular TCE and ^{13}C TCE. Results of analysis confirmed that CM was not a direct product of TCE dechlorination at the granular graphite cathode that *cis*-DCE was an intermediate product of TCE dechlorination, and that 1,1-DCE was not a dechlorination product.
Published by Elsevier B.V.

Keywords: Carbon stable isotope; Trichloroethylene (TCE); Electrolytic dechlorination

1. Introduction

Trichloroethylene (TCE) was effectively dechlorinated in ammonium acetate solutions using granular graphite electrodes in a mixed electrochemical reactor, and the major chlorine-containing product was chloromethane (CM) [1,2], a possible carcinogen. The formation of CM was hypothesized as a product of TCE dechlorination through carbon-carbon breakage [1], but this hypothesis need to be confirmed experimental investigation in order to fully understand this promising remediation technology and to minimize CM production. One of the techniques to do this is the use of stable isotope compounds.

Use of stable isotopes is still a new and developing technique to study the fate and transport of contaminants in the environment [3–7]. For example, stable isotope compounds were used to study the microbial dechlorination of chlorinated hydrocarbons [8–12]. Stable isotope TCE was used to study isotope fraction-

ation in the physical process of vaporization of TCE [13] and in the reductive dechlorination of TCE by zero-valent iron [14]. However, the uses of stable isotopes in these studies (of isotope fractionation) are limited because analysis of these compounds requires special mass spectrometry.

Stable isotope analysis is commonly facilitated by gas chromatography/isotope ratio mass spectrometry (GC/IRMS) [15,16]. Isotopic composition is usually presented with a ratio, δ ^{13}C, which is a measure of the ratio of the two stable isotopes of carbon present in a sample with respect to the ratio of the two stable isotopes of carbon in a standard reference material. Isotopic fractionation, measured with a fractionation factor α, occurs when δ ^{13}C changes during physical, chemical, or biological processes. Details of various stable isotope analytical techniques and comprehensive discussion of isotope fractionation are available in the literature [17,18].

The purpose of this study was to investigate the formation of CM during the TCE dechlorination at granular graphite electrodes. The objectives were (1) to develop a method to use a conventional GC/MS for the analysis of TCE and other chlorinated hydrocarbons compounds that possess a carbon stable isotope and (2) to investigate the formation of CM and

---

* Corresponding author. Tel.: +1 513 569 7849; fax: +1 513 569 7879.
E-mail address: Al-Abed.Souhail@epa.gov (S.R. Al-Abed).

obtain further understanding of the mechanism of electrolytic dechlorination of TCE at granular graphite electrodes.

2. Experimental methods

2.1. Chemicals

Chemicals used were trichloroethylene, >99% (Aldrich, Milwaukee, WI, USA); carbon stable isotope TCE (^{13}C TCE), (Cl$_2$ ^{13}C=^{13}CHCl, 99%) (Cambridge Isotope Laboratory, Andover, MA, USA); ammonium acetate (ACS cert., Fisher, Pittsburgh, PA, USA.); sodium azide (Fisher, Lab. grade), granular graphite (Fisher, 30–50 mesh), benzene-D6 (Sigma, St. Louis, MO, USA). Standards of chlorinated organic compounds were QTM Volatile Halocarbons Mix (No. 48001, Supelco, Bellefonte, PA, USA) and VOC Mix 6 (Supelco No. 4S8799). Aqueous standards were prepared by mixing the chlorinated organic standards in milli-Q water (resistivity $\geq$18 MΩ cm). The gas standards for methane, ethane, ethylene, and acetylene were from Scott Specialty Gases. The internal gas standard of 5000 ppmv (parts per million by volume) benzene-D6 in nitrogen was prepared by injecting 21 μL benzene-D6 liquid into 1 L N$_2$ at 101 kPa.

2.2. Experimental setup and procedures

The electrolytic dechlorination experiments were conducted in the reactor system schematically shown in Fig. 1. The electrolytic reactor consisted of a packed bed of 55 g granular graphite (300–600 μm) as the cathode and an anode of two-pieces of platinum wire gauze. The packed bed reactor was connected through a Teflon tube to a solution tank, in which 160 mL of 0.1 M ammonium acetate electrolyte solution was mixed continuously with a magnetic-bar. The system solution was circulated between the tank and the reactor via a peristaltic pump. The headspace of the solution tank was connected to a gas tank, which was a gastight 1 L syringe that was able to expand at a pressure increase of less than 20 kPa, to collect gases generated during the experiment and to keep the system at a constant pressure.
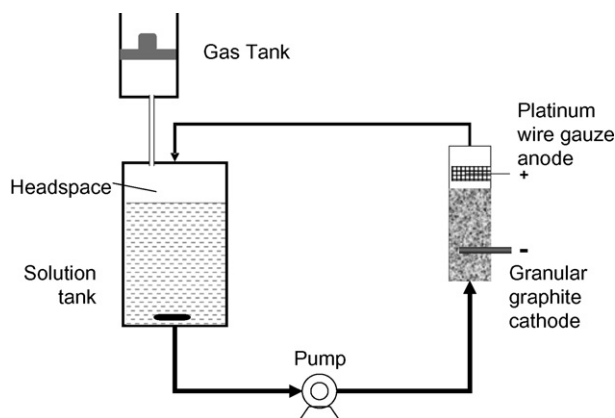

Fig. 1. Schematic diagram of the electrochemical reactor system for TCE reductive dechlorination.

After the same volumes of pure regular TCE and ^{13}C TCE were injected into the solution, it was completely mixed to reach equilibrium between the solution and the headspace gas. The electrolytic dechlorination began once a constant current of 50 mA was flowing through the electrodes and the solution was circulated at a flow rate of 7.6 mL/min.

During the experiment, samples were taken periodically from the solution and the headspace gas for the analyses of chloride in the solution, hydrocarbons in the headspace, and chlorinated hydrocarbons in both the solution and the headspace. The chlorinated hydrocarbons include TCE and possible dechlorination products and they were analyzed using the EPA SW-846 method 8260 for volatile organic compounds. The solution samples for chlorinated hydrocarbons were injected with an internal standard, which was benzene-D6 in methanol, and the samples were then placed in the automatic headspace sampler, and analyzed by a GC/MS, which was coupled with the automatic headspace sampler. For each headspace analysis for chlorinated hydrocarbons, a 25 μL of gas sample was combined with a 25 μL internal standard gas, which was benzene-D6 in nitrogen, and then the combined gas was directly injected into the GC/MS. The headspace samples were analyzed with a method similar to the GC/MS method for the solution samples but were quantified using a different set of calibration curves. The method's detection limits were 0.5 mg/L for all the components in the solution, and 34 ppmv for TCE and 9 ppmv for other chlorinated compounds in headspace samples [19].

The hydrocarbons were methane, ethane, ethylene, and acetylene, and they were analyzed using a method based on EPA method 8015 for nonhalogenated organics with a flame ionization detector (FID) equipped HP 6890 GC. Chloride analysis was conducted with a Waters capillary ion analyzer (CIA) using the solutions left from the solution samples for dechlorinated hydrocarbons.

2.3. Analysis and quantification of ^{13}C compounds

Samples of the solutions and headspaces were analyzed using the conventional GC/MS and the abundances of ion fragments from both regular and carbon stable isotopes were collected for TCE and possible chlorinated products. These fragments for TCE, DCE isomers, and CM are listed in Table 1. These fragment responses, illustrated in Fig. 2 for TCE and in Fig. 3 for

Table 1

m/z values for MS peaks collected for the chlorinated compounds of ^{12}C and ^{13}C carbon isotopes

	^{12}C compounds only[a]	^{12}C and ^{13}C compounds[b]	^{13}C compounds only
TCE$_{12}$	130	132	
TCE$_{13}$		132	134
DCE$_{12}$	96	98	
DCE$_{13}$		98	100
CM$_{12}$	50	51	
CM$_{13}$		51	52

[a] Peaks are collected for quantification of regular compounds.
[b] Peaks are collected for quantification of ^{13}C isotope compounds.
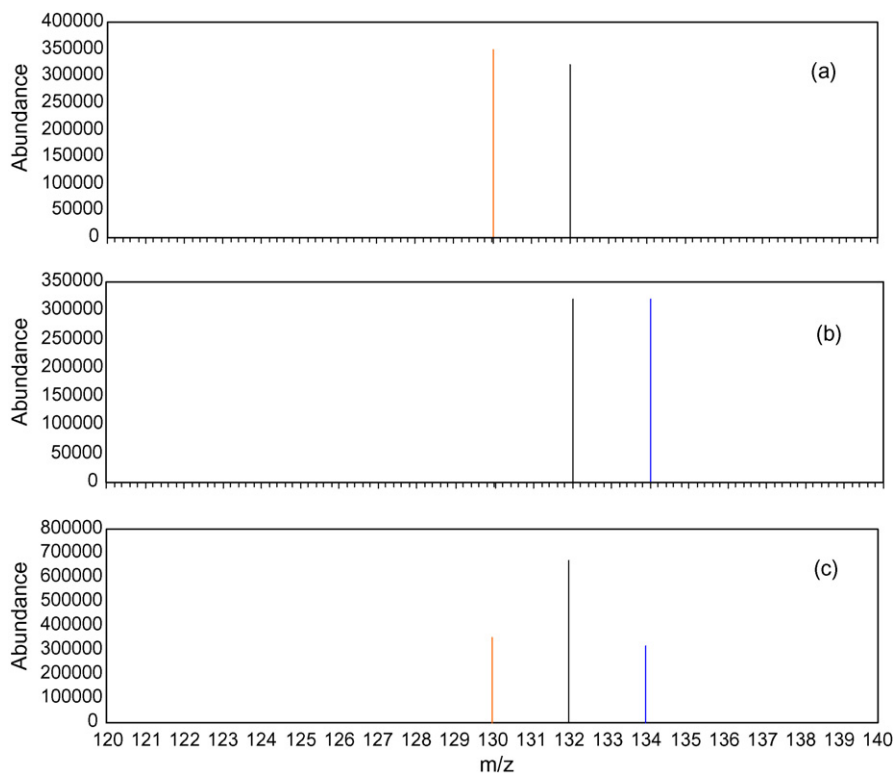
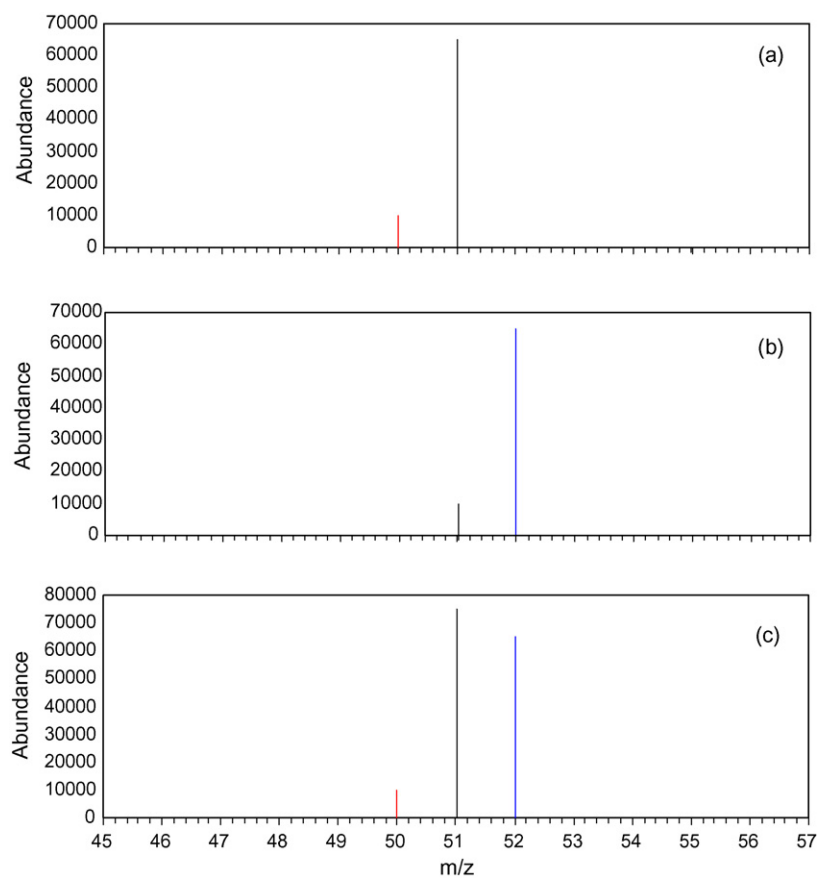Fig. 2. Spectra of regular TCE (a), carbon stable isotope TCE (b), and of both at a molar ratio 1:1 (c).

Fig. 3. Spectra of regular CM (a), carbon stable isotope CM (b), and of both at a molar ratio 1:1 (c).

chloromethane, were verified in the GC/MS spectra using the Scan mode and collected for quantification using the Sim mode. For a regular isotope, the concentration in standards and samples were quantified based on the abundance of its fragment with the lowest mass per charge. The concentration of a carbon stable isotope compound could not be directly calculated based on the abundance of the lower mass fragment because part of its abundance came from the regular compound.

The presence of ^{13}C compounds can be represented using a relative ratio (β) of the mid-mass (both ^{12}C and ^{13}C compounds contributes to the peak) to the low mass (only ^{12}C compound contributes to the peak).

$$\beta = \frac{([^M A]/[^L A])_{\text{sample}}}{([^M A]/[^L A])_{\text{regular standard}}} \tag{1}$$

where $[^L A]$ and $[^M A]$ are the abundances of the low mass species $^L A$ and the mid mass species $^M A$, respectively; the ratio in the denominator is obtained by using check standards that contain only regular chlorinated compounds; and the ratio in the numerator is obtained from samples that contain both regular and ^{13}C carbon isotopes.

The quantification method is developed in the following section.

3. Results and discussion

3.1. Calculation of ^{13}C TCE Concentration

For a sample that contains ^{13}C TCE:TCE at a molar ratio of x:1, the fragment abundances of ^{13}C TCE and regular TCE are illustrated in Table 2. Therefore, the β ratio for TCE in the sample is

$$\beta = \frac{([^{132}\text{TCE}_{12}] + x[^{132}\text{TCE}_{13}]/[^{130}\text{TCE}_{12}])_{\text{sample}}}{([^{132}\text{TCE}_{12}]/[^{130}\text{TCE}_{12}])_{\text{standard}}} \tag{2}$$

where $[^{130}\text{TCE}_{12}]$ and $[^{132}\text{TCE}_{12}]$ are the abundances of fragments $^{130}\text{TCE}_{12}$ and $^{132}\text{TCE}_{12}$ from regular TCE at $m/z = 130$ and 132, respectively; $x[^{132}\text{TCE}_{13}]$ is the abundance of fragment $^{132}\text{TCE}_{13}$ at $m/z = 132$ from the ^{13}C TCE in the sample; $[^{132}\text{TCE}_{13}]$ is the abundance of fragment $^{132}\text{TCE}_{13}$ from ^{13}C TCE in a solution in which $x=1$. Because the ratio of $[^{132}\text{TCE}_{12}]$:$[^{130}\text{TCE}_{12}]$ in a standard should be the same as the

Table 2
Responses of fragments from a sample with a ^{13}C TCE to regular TCE ratio of x:1

m/z	Abundance		
	TCE[a] (1)	^{13}C TCE[a] (x)	TCE + ^{13}C TCE[a] ($1+x$)
130	$[^{130}\text{TCE}_{12}]$		$[^{130}\text{TCE}_{12}]$
132	$[^{132}\text{TCE}_{12}]$	$x[^{132}\text{TCE}_{13}]$	$[^{132}\text{TCE}_{12}] + x[^{132}\text{TCE}_{13}]$
134		$x[^{134}\text{TCE}_{13}]$	$x[^{134}\text{TCE}_{13}]$

Value in parentheses represent molar ratio.
[a] Compounds.

ratio for regular TCE in a sample,

$$\left(\frac{[^{132}\text{TCE}_{12}]}{[^{130}\text{TCE}_{12}]}\right)_{\text{standard}} = \left(\frac{[^{132}\text{TCE}_{12}]}{[^{130}\text{TCE}_{12}]}\right)_{\text{sample}} \tag{3}$$

Eq. (2) can be rewritten as:

$$\beta - 1 = \left(\frac{x[^{132}\text{TCE}_{13}]}{[^{132}\text{TCE}_{12}]}\right)_{\text{sample}} = x\frac{[^{132}\text{TCE}_{13}]}{[^{132}\text{TCE}_{12}]} \tag{4}$$

where $[^{132}\text{TCE}_{13}/^{132}\text{TCE}_{12}]$ is the response ratio of fragments $^{132}\text{TCE}_{13}$ and $^{132}\text{TCE}_{12}$ respectively from ^{13}C TCE and regular TCE at the same concentration, and its value is independent of the sample composition (x) and is a characteristic response (parameter) to the compounds by MS. (The derivation of Eq. (4) assumed a linear response by the MS detector to the isotope compound in the interested concentration range.)

Eq. (4) can be further transformed into Eq. (5) to calculate the concentration of ^{13}C TCE in the solution in terms of the concentration of regular TCE.

$$x = (\beta - 1)\frac{[^{132}\text{TCE}_{12}]}{[^{130}\text{TCE}_{12}]}\frac{[^{130}\text{TCE}_{12}]}{[^{132}\text{TCE}_{13}]} \tag{5}$$

The concentration ratio (x) can thus be determined from the response ratio, β, and two characteristic spectrum ratios. The ratio $[^{132}\text{TCE}_{12}/^{130}\text{TCE}_{12}]$ is 0.92, which was obtained from the MS spectrum of regular TCE and from the analysis of a check standard that contained only regular TCE. The value of the ratio $[^{130}\text{TCE}_{12}/^{132}\text{TCE}_{13}]$, which is the relative abundances of $^{130}\text{TCE}_{12}$ of the regular TCE to the abundance of its counterpart ($^{132}\text{TCE}_{13}$) of ^{13}C TCE, can be calculated based on the responses of these fragments from analysis of standard samples of regular and ^{13}C TCE at a given concentration. In this study, the value of $[^{130}\text{TCE}_{12}/^{132}\text{TCE}_{13}]$ was obtained from the responses of the fragments from the TCE compounds in the first sample, in which the molar ratio (x) was 1 (because the same volume of regular and ^{13}C TCE were injected in the initial solution). The measured value of β from the first sample was 1.93, therefore, $[^{130}\text{TCE}_{12}/^{132}\text{TCE}_{13}] = 1.1688$.

Table 3 lists the results of GC/MS analysis of the solution samples. The responses of ^{132}TCE were contributions from both $[^{132}\text{TCE}_{12}]$ and $[^{132}\text{TCE}_{13}]$. The values of β (and $\beta - 1$) and x were calculated from Eq. (1) and Eq. (5), respectively. The average of the ($\beta - 1$) values is 0.94 with a standard deviation of 0.008, and the average of x is 1.01 with a standard deviation of 0.009 (sample size = 9).

The decreases in the peak responses and the consistent value of the β ratio indicate that both ^{13}C TCE and regular TCE were dechlorinated simultaneously at the same rate in the reactor. Fig. 4 shows the profiles of concentrations of regular TCE, ^{13}C TCE, and their total in the solutions. The concentration of regular TCE in a sample was quantified based on $[^{130}\text{TCE}_{12}]$, and the concentration of ^{13}C TCE in the sample was calculated by multiplying x by the regular TCE concentration.

Table 3
Responses and values of β, $\beta - 1$, x for chlorinated organic compounds (^{12}C and ^{13}C) in the samples

Time (h)	TCE					cis-DCE		1,1-DCE		CM		
	[^{130}TCE]	[^{132}TCE][a]	β	$\beta - 1$	x[b]	$\beta - 1$	x[c]	$\beta - 1$	x[c]	^{51}CM:^{50}CM	$\beta - 1$	x[c]
0	6971782	12319251	1.93	0.93	1.00			0.63	0.39			
1	4836959	8572805	1.94	0.94	1.01	1.61	1.00	0.49	0.31			
3	3011261	5352521	1.94	0.94	1.01	1.41	0.87	0.36	0.23	7.23	0.12	0.79
5	1826938	3246530	1.94	0.94	1.01	1.16	0.72	0.04	0.03	6.42	0.00	−0.02
5[d]	1698700	3033828	1.95	0.95	1.02	0.91	0.56	0.11	0.07	6.37	0.01	−0.07
7	1111957	1981949	1.95	0.95	1.00	1.29	0.80	0.07	0.04	6.42	0.00	−0.02
9	378920	669722	1.93	0.93	1.00	1.04	0.64	0.18	0.11	6.49	0.01	0.05
11	400241	707294	1.93	0.93	1.00	1.38	0.86	0.01	0.01	6.46	0.00	0.01
13	248064	437882	1.93	0.93	1.02	0.86	0.53	0.09	0.06	6.02	0.07	−0.42

[a] The abundances include both [^{132}TCE$_{12}$] and [^{132}TCE$_{13}$].
[b] Calculated based on [^{132}TCE$_{12}$]/[^{130}TCE$_{12}$] = 0.92 and [^{130}TCE$_{12}$]/[^{132}TCE$_{12}$] = 1.1688.
[c] Estimated based on [^{98}DCE$_{12}$]/[^{96}DCE$_{13}$] = 0.62, [^{51}CM$_{12}$]/[^{50}CM$_{13}$] = 6.44, and [$^{L}A_{12}$]/[$^{M}A_{13}$] ≈ 1 for CM and DCE isomers.
[d] Duplicate sample.

3.2. cis-DCE and 1,1-DCE

The concentrations of cis-DCE and 1,1-DCE that possess carbon stable isotopes can also be calculated using the method presented in previous section. For any compound (listed in Table 1) present in a sample at a regular to ^{13}C isotope molar ratio 1:x, the relationships between β and x are

$$\beta - 1 = \left(\frac{x[^{M}A_{13}]}{[^{M}A_{12}]} \right)_{\text{sample}} \tag{6}$$

$$x = (\beta - 1) \frac{[^{M}A_{12}]}{[^{L}A_{12}]} \frac{[^{L}A_{12}]}{[^{M}A_{13}]} \tag{7}$$

where [$^{L}A_{12}$] and [$^{M}A_{12}$] are the abundances of fragments $^{L}A_{12}$ and $^{M}A_{12}$ from the ^{12}C compound at $m/z = L$ and $m/z = M$, respectively; $x[^{M}A_{13}]$ is the abundance of fragment $^{M}A_{13}$ at $m/z = M$ from the ^{13}C compound in the sample; [$^{M}A_{13}$] is the abundance of fragment $^{M}A_{13}$ at $m/z = M$ from the ^{13}C compound at the same concentration as that of the ^{12}C compound in the sample. Values of β and [$^{M}A_{12}$/$^{L}A_{12}$] were obtained from peak abundances of the compound in samples (with the isotope compound) and in check standards (without the isotope compound), respectively. The values of $\beta - 1$ indicate the actual contribution from the ^{13}C compound to the peak at $m/z = M$, but calculating the concen-

Fig. 4. Concentration profiles of ^{13}C isotope TCE and regular TCE.

trations of ^{13}C compounds in the samples requires the values of [$^{L}A_{12}$/$^{M}A_{13}$].

The values of [$^{L}A_{12}$/$^{M}A_{13}$] can be calculated based on the abundances of these fragments from (standard) samples of regular and ^{13}C compounds at the same concentrations. Such ^{13}C compounds, except TCE, were not available in our experiments. However, because of the similarities of the two isotope compounds (in their nature and in residence time) and because of the close values of the mass per change of these fragment (the differences are only 1 or 2), the values of [$^{L}A_{12}$/$^{M}A_{13}$] should not be much different from 1, as indicated in the measured value for TCE (1.1688). Therefore, in estimating the concentrations of the ^{13}C compounds in the samples, the values of [$^{L}A_{12}$/$^{M}A_{13}$] were taken as 1 for CM and DCE isomers.

The concentrations of cis-DCE and 1,1-DCE in the solution samples were not quantified because their values were below the method detection limits. However, their peaks at their characteristic residence times were detected and identified, and the abundances of fragments at $m/z = 96$ and 98 were collected. For cis-DCE, these fragment abundances were used to calculate the values of β and $\beta - 1$, listed in Table 3, based on the ratio ^{98}DCE$_{12}$:^{96}DCE$_{12}$, which was 0.62. The average value of $\beta - 1$ for cis-DCE is 1.21 with a standard deviation of 0.263. The relative large standard deviation was a result of MS responses at the very low concentration of cis-DCE in the samples. The fact that cis-DCE was not detected in the first sample but was detected in the later samples indicates that that ^{13}C cis-DCE was formed as an intermediate product during the dechlorination of ^{13}C TCE. Table 3 also lists the x values for cis-DCE estimated using Eq. (7).

For 1,1-DCE, Table 3 lists the values of $\beta - 1$ and the estimates of x. The values of x and $\beta - 1$ decreased over time and were approximately zero after the third sample. In contrast to cis-DCE, 1,1-DCE was present in the initial solution, which indicates that 1,1-DCE was introduced into the system through the TCE stock solution. These results indicate that 1,1-DCE was not formed during TCE dechlorination. A decrease in the x values suggests that ^{13}C 1,1-DCE was removed from the solution faster than the regular 1,1-DCE.

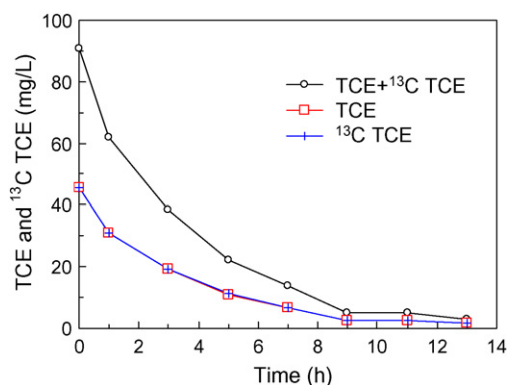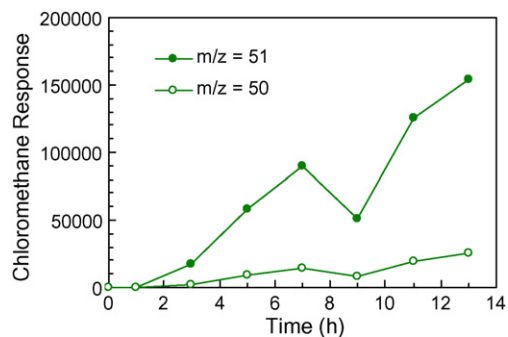Fig. 5. Chloromethane abundances at peaks $m/z = 50$ and 51.

3.3. Chloromethane

The abundances of CM fragments at $m/z = 50$ and $m/z = 51$ were collected and were plotted versus time in Fig. 5. From these data, the values of β and $\beta - 1$ were calculated, based on the ratio of $^{51}CM_{12}$:$^{50}CM_{12}$ (=6.44) which was obtained from a standard of regular chlorinated compounds. Table 3 lists the values of $\beta - 1$ and the estimates of x. The average of $\beta - 1$ is 0.01 with a standard deviation of 0.06, and the average of x is 0.03 with a standard deviation of 0.32. These results suggest a zero contribution of fragment $^{51}CM_{13}$ from possible ^{13}C CM to the peak at $m/z = 51$. Therefore, ^{13}C CM was not formed in the system during the dechlorination of regular TCE and ^{13}C TCE, which leads to the conclusion that the carbon for chloromethane did not come from breakage of the carbon–carbon bond of TCE.

On the other hand, CM was formed as chloride was rapidly consumed in an electrolytic experiment in a 0.1 M NH$_4$Ac solution that contained no TCE but 2.35 mM KCl. The result of the experiment, which was conducted at an applied cell potential of 10 V in the same reactor system, confirmed that the chloride reacted in the reactor to form CM. Furthermore, acetate was proved to be the carbon source for the formation of CM because no CM was detected in a TCE dechlorination experiment when potassium nitrate was used as the electrolyte to replace ammonium acetate. These results confirmed that CM was formed as a result of electrode reactions of the chloride and acetate at the anode, in a so-called Kolbe reaction where acetate is oxidized to a methyl radical, which combined with a chlorine radical to form chloromethane [20].

3.4. Dechlorination of ^{13}C TCE and regular TCE

Table 4 summarizes the amounts of TCE and dechlorination products in the three phases—the solution, the headspace, and gas tank at the end of the 13-h experiment. Results presented in Table 4 and Fig. 4 show that the total concentration of regular and ^{13}C TCE decreased from 90.8 mg/L to final 3.0 mg/L, resulting in 96.7% of the TCE removal from the solution, with only 7.1% of the TCE in the reactor at the end of the experiment. Two DCE isomers, *cis*-DCE and 1,1-DCE, were detected but were not quantified because their concentrations were below the method's detection limits. Analysis of DCE isomers of regular and ^{13}C isotopes indicated that *cis*-DCE was an intermediate

Table 4
Compounds in the reactor presented as calculated from the amount of chlorine[a]

	Solution	Headspace	Gas tank	Total
Initial	331.9	9.8	0.0	341.7
End				
TCE	10.56	0.27	12.63	23.46
CM	8.54	0.44	3.21	12.19[b]
Cl$^-$	131.9	0	0	131.9
Cl in organics	19.1	0.71	15.84	35.65
Cl$^-$ (%)	38.6			38.6[b]
Cl in organics (%)	5.8	0.2	4.6	10.6[b]

[a] *cis*-DCE and 1,1-DCE were detected but were not quantified because their concentrations were below the method's detection limits. The units are μmol for all the numbers except the percentages.

[b] Total amount of CM was about 3.8% of the total chlorine in the initial reactor. If CM was prevented, the Cl in organics (%) and Cl$^-$ (%) would be 7.0% and 42.2%, respectively.

product of TCE dechlorination and that 1,1-DCE was initially in the solution and was dechlorinated during the experiment. About 3.6% of chlorine in the initial TCE ended up in CM; its formation could have been prevented by using electrolytes other than acetate.

Fig. 6 shows the distribution of chlorine in the different phases in the reactor. The majority of chlorine in the initial TCE ended up as chloride in the solution. Table 4 shows that chloride in the solution was 38.6% of the initial chlorine in the TCE. If the part of chlorine in CM were considered as chloride, then the chloride amount would be 42.2% of the initial chlorine in TCE, which indicates that at least 42.2% of TCE was dechlorinated.

The majority of the carbon from the initial TCE ended up as ethane in the gas tank. Its amounts in the headspace and the tank were 10.3 μmol and 148.6 μmol, respectively. The amounts of ethylene were 0.07 μmol and 1.3 μmol, respectively, in the headspace and in the tank. The total amount of acetylene was less than 0.06 μmol. The total of these hydrocarbons at the end is more than that contributed from the initial 113.9 μmol of TCE, which was a result of the production of these compounds from the surface reactions of acetate at the granular graphite electrode. $[2CH_3COO^- -2e \rightarrow CO_2 + 2CH_3;\ 2CH_3 \rightarrow C_2H_6]$

A total of 49.3% of chlorine was recovered at the end, which was commonly observed in the TCE dechlorination in such a reactor using granular graphite electrodes. The major loss of
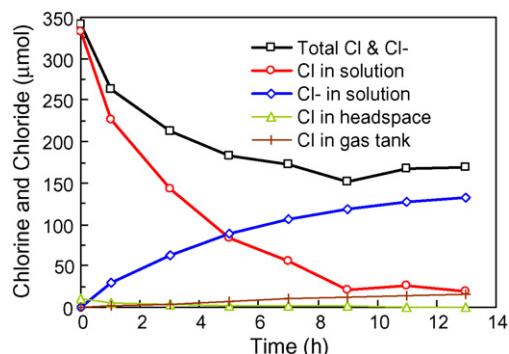

Fig. 6. TCE dechlorination and chlorine mass distribution inside the reactor.

chlorine was due to the adsorption of TCE on the granular graphite. Control experiments conducted without electric power applied to the reactor demonstrated that about 30% of TCE can be adsorbed by the granular graphite inside the reactor. In addition, it is likely that chloride may have reacted at the anode to cause some loss of chlorine during the experiment. These topics need to be addressed in future publications.

4. Conclusions

A method was developed to use a conventional GC/MS to estimate and differentiate between the peak contributions of isotope fragments from regular fragments and to analyze regular and carbon stable isotope compounds. The concentration of a ^{13}C compound can be calculated, based on the concentration of its regular compound, from the response ratio of two fragments of different mass per charge values from the compounds in a sample and two characteristic MS spectrum ratios: one is the response ratio of the two fragments of the regular compound, and the other is the response ratio of the corresponding fragments of the regular and ^{13}C compounds at the same concentrations. This method was successfully applied to the analyses of regular and ^{13}C compounds in the dechlorination of regular and ^{13}C TCE.

CM was not formed through the breakage of the carbon-carbon bond of the TCE molecule because ^{13}C CM was not formed during the electrolytic dechlorination of regular TCE and carbon stable ^{13}C TCE. Instead, CM was formed through the reaction of chloride with the acetate ion at the anode. In addition, results of isotope fragment analysis indicate that *cis*-DCE was an intermediate product of TCE dechlorination while 1,1-DCE was not.

Due to the availability of conventional mass spectroscopy, this method has a high potential of being used to investigate reaction mechanisms and to study the fate and transport of contaminants in the environment. This method is not suitable for studying the subtle effects of fractionation of trace isotopes because a conventional MS is not as sensitive and accurate as an IRMS, however, the theory developed in this paper can be equally applied to the analysis of isotope spectra from an IRMS.

References

[1] J.L. Chen, S.R. Al-Abed, J.A. Ryan, A. Li, Groundwater and soil remediation using electrical fields, in: L.R.Lipnick, R.P. Mason, M.L. Phillips, C.U. Pittman (Eds.), ACS Symposium Series 806, Chemicals in the Environment, American Chemical Society, Washington, DC, 2002, pp. 434–448.

[2] Y. Fang, S.R. Al-Abed, V. Kukainis, Electrochemical dechlorination of trichloroethylene using granular-graphite electrodes: identification and quantification of dechlorination products, in: American Chemical Society 225th Annual Meeting, New Orleans, LA, 2003, pp. 748–753.

[3] G.F. Slater, J.M.E. Ahad, B.S. Lollar, R. Allen-King, B. Sleep, Carbon isotope effects resulting from equilibrium sorption of dissolved VOCs, Anal. Chem. 72 (2000) 5669–5672.

[4] B.S. Lollar, G.F. Slater, B. Sleep, M. Witt, G.M. Klecka, M. Harkness, J. Spivack, Stable carbon isotope evidence for intrinsic bioremediation of tetrachloroethene and trichloroethene at area 6, dover air force base, Environ. Sci. Technol. 35 (2001) 261–269.

[5] S.R. Poulson, H. Naraoka, Carbon isotope fractionation during permanganate oxidation of chlorinated ethylenes (CDCE, TCE, PCE), Environ. Sci. Technol. 36 (2002) 3270–3274.

[6] S. Dousset, J. Leveque, S. Jault, M.J. Milloux, F. Andreux, Assessing the transfer of pentachlorophenol through soil columns using ^{13}C isotope, Sci. Total Environ. 291 (2002) 99–104.

[7] P.L. Morrill, G. Lacrampe-Couloume, G.F. Slater, B.E. Sleep, E.A. Edwards, M.L. McMaster, D.W. Major, B.S. Lollar, Quantifying chlorinated ethene degradation during reductive dechlorination at Kelly AFB using stable carbon isotopes, J. Contam. Hydrol. 76 (2005) 279–293.

[8] J.J. Drenzek, T.I. Eglinton, C.O. Wirsen, N.C. Sturchio, L.J. Heraty, K.R. Sowers, Q. Wu, H.D. May, C.M. Reddy, Invariant chlorine isotopic signatures during microbial PCB reductive dechlorination, Environ. Pollut. 128 (2004) 445–448.

[9] S.B. Lollar, G.F. Slater, J. Ahad, B. Sleep, J. Spivack, M. Brennan, P. MacKenzie, Contrasting carbon isotope fractionation during biodegradation of trichloroethylene and toluene: implications for intrinsic bioremediation, Org. Geochem. 30 (1999) 813–820.

[10] G.F. Slater, B.S. Lollar, B.E. Sleep, E.A. Edwards, Variability in carbon isotopic fractionation during biodegradation of chlorinated ethenes: implications for field applications, Environ. Sci. Technol. 35 (2001) 901–907.

[11] D.L. Song, M.E. Conrad, K.S. Sorenson, L. Alvarez-Cohen, Stable carbon isotope fractionation during enhanced in situ bioremediation of trichloroethene, Environ. Sci. Technol. 36 (2002) 2262–2268.

[12] R.U. Meckenstock, B. Morasch, C. Griebler, H.H. Richnow, Stable isotope fractionation analysis as a tool to monitor biodegradation in contaminated acquifers, J. Contam. Hydrol. 75 (2004) 215–255.

[13] S.R. Poulson, J.I. Drever, Stable isotope (C, Cl, H) fractionation during vaporization of trichloroethylene, Environ. Sci. Technol. 33 (1999) 3689–3694.

[14] G.F. Slater, B.S. Lollar, R.A. King, S. O'Hannesin, Isotopic fractionation during reductive dechlorination of trichloroethene by zero-valent iron: influence of surface treatment, Chemosphere 49 (2002) 587–596.

[15] C.R. McKinney, J.M. McCrea, S. Epstein, H.A. Allen, H.C. Urey, Improvements in mass spectrometers for the measurement of small differences in isotope abundance ratios, Rev. Sci. Intrum. 21 (1950) 724–730.

[16] K.H. Freeman, J.M. Hayes, J.M. Trendel, P. Albrecht, Evidence from carbon isotope measurements for diverse origins of sedimentary hydrocarbons, Nature 343 (1990) 254–256.

[17] W.S. Broecker, V.M. Oversby, Chemical Equilibria in the Earth, McGraw-Hill, New York, 1971.

[18] P.A. de Groot (Ed.), Handbook of Stable Isotope Analytical Techniques, vol. I, Elsevier Science, 2004.

[19] Y. Fang, S.A. Al-Abed, Use of granular graphite for electrolytic dechlorination of trichloroethylene. Environ. Eng. Sci., in press.

[20] A.C. Brown, J. Walker, Ann. Chem. 261 (1891) 107.