

GC/Multiple Collector-ICPMS Method for Chlorine Stable Isotope Analysis of Chlorinated Aliphatic Hydrocarbons

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Stable isotopic characterization of chlorine in chlorinated aliphatic pollution is potentially very valuable for risk assessment and monitoring remediation or natural attenuation. The approach has been underused because of the complexity of analysis and the time it takes. We have developed a new method that eliminates sample preparation. Gas chromatography produces individually eluted sample peaks for analysis. The He carrier gas is mixed with Ar and introduced directly into the torch of a multicollector ICPMS. The MC-ICPMS is run at a high mass resolution of $\geq 10\,000$ to eliminate interference of mass 37 ArH with Cl. The standardization approach is similar to that for continuous flow stable isotope analysis in which sample and reference materials are measured successively. We have measured PCE relative to a laboratory TCE standard mixed with the sample. Solvent samples of 200 nmol to 1.3 μmol (24–165 μg of Cl) were measured. The PCE gave the same value relative to the TCE as measured by the conventional method with a precision of 0.12‰ (2 \times standard error) but poorer precision for the smaller samples.

Background. Chlorinated aliphatic hydrocarbons (CAHs), such as trichloroethene (TCE) and tetrachloroethene (perchloroethylene or PCE), have been extensively used in many industries for their degreasing properties since the 1940s. Because of careless disposal and leakages, CAHs are widespread groundwater pollutants, where they tend to remain for relative long periods of time.¹ It is possible to characterize CAH natural attenuation by the stable isotopic compositions of carbon and chlorine.^{2,3} Variations in $^{37}\text{Cl}/^{35}\text{Cl}$ are expressed as parts per thousand differences from SMOC (Standard Mean Ocean Chloride), used internationally as the standard.^{4–7}

Two types of method are available presently to determine stable chlorine isotope ratios, some using gas-source stable isotope ratio mass spectrometry (SIRMS, giving ratios relative to a reference material) and others based on thermal ionization mass spectrometry (TIMS). These methods rely on the conversion of the chlorine-bearing molecules into inorganic chlorine by combustion, by chemical reaction, or both.^{8–11} The inorganic chlorine so produced by combustion or chemical reduction is converted into AgCl and subsequently CH_3Cl for SIRMS or CsCl for TIMS analysis.¹² Additional cryogenic or chromatographic purification steps are usually necessary prior to analysis. Any method must ensure not only high precision, but also accuracy; the chlorine in the compound analyzed should consist only of all the chlorine of the original sample. Yields of Cl less than 100% from the conversion reactions may produce variable isotopic fractionation. There also should be a negligible contribution from the blank Cl. The sensitivity of the TIMS method is 10 μg with a $^{37}\text{Cl}/^{35}\text{Cl}$ reproducibility on the order of 0.3 ‰. For SIRMS, the minimum sample size is $\sim 140\ \mu\text{g}$ of chlorine with a reproducibility of 0.08 ‰.¹³

The conversion and purification steps associated with SIRMS and TIMS are time-consuming and, therefore, costly. The high cost has led to an underuse of chlorine isotopes as tracers in environmental studies.¹⁴ The sensitivity of these methods is another drawback because relatively large volumes of CAHs (on the order of 1 μL) and, consequently, large volumes of contami-

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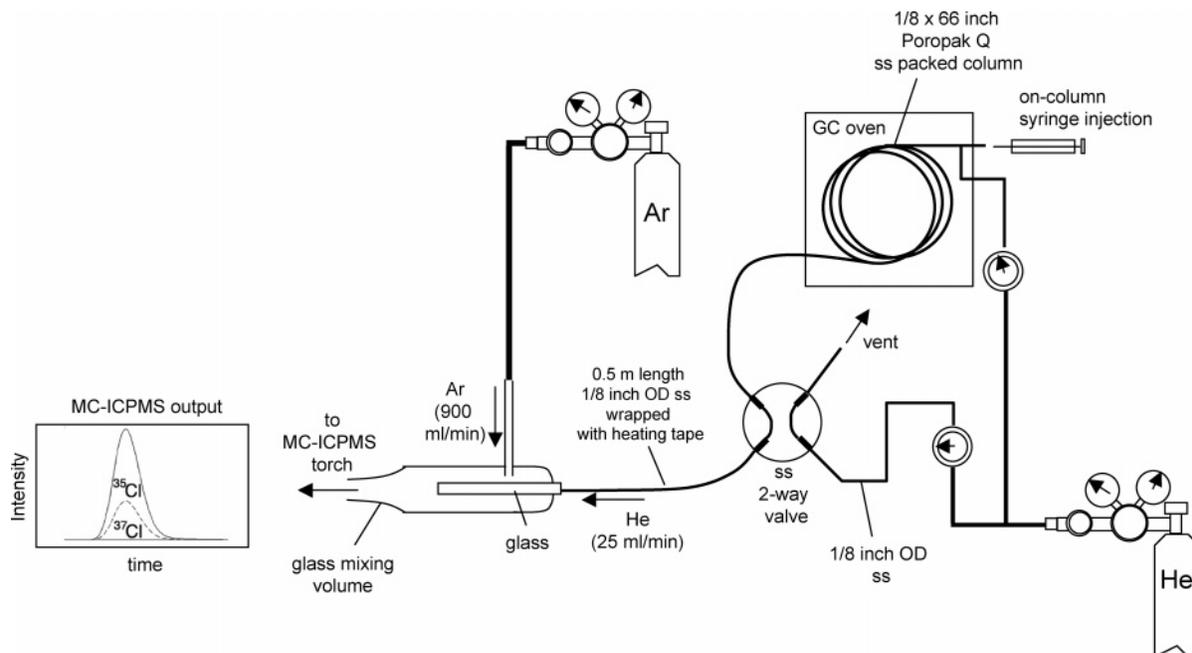


Figure 1. Schematic diagram of the GC/MC-ICPMS and connecting line.

nated groundwater are required for analysis. These constraints led us to develop a new method that would reduce the time for analysis without decreasing sensitivity.

Rationale for Method Development. We investigated the use of multiple collector inductively coupled plasma-source mass spectrometry (MC-ICPMS) as a tool for measuring $^{37}\text{Cl}/^{35}\text{Cl}$ in CAHs because of its exceptional sensitivity for a large range of elements, the possibility of avoiding expensive sample preparation, and the high precision for light element stable isotope ratio measurements afforded by MC-ICPMS. Our approach was to couple a gas chromatograph to the front end of an MC-ICPMS instrument as a means for separating and purifying the analyte prior to isotopic analysis. The benefits of such an approach had been described previously.¹⁵

There were some immediately apparent problems to be overcome in applying MC-ICPMS to Cl isotope ratio analysis. Chlorine has a high first ionization potential (13.01 eV), meaning that the ionization yield is low (1% or less) in comparison to many other elements (usually >50%). Additionally, $^1\text{H}^{36}\text{Ar}^+$ produced in the Ar plasma is a significant mass-to-charge (m/z) interference for $^{37}\text{Cl}^+$.

In this paper, we show how we overcame the potential problems and present the results of a new, sensitive method for the determination of stable chlorine isotope ratios of CAH mixtures by GC separation followed by on-line continuous flow MC-ICPMS (GC/MC-ICPMS).

EXPERIMENTAL SECTION

Equipment. A gas chromatograph (SRI 8610C, SRI Instruments, USA) fitted with a Poropak Q packed column (1/8" x 6 feet) and a thermal conductivity detector (TCD) was used to separate CAH species. A He carrier gas was used at a pressure corresponding to a flow rate of 26 mL/min exiting the column.

The column temperature was varied from 160 to 180 °C for elution of TCE and PCE, respectively.

The gas chromatograph (GC) was coupled to the MC-ICPMS by means of a stainless steel tube (Figure 1). The transfer line was heated with a heating sleeve (~100 °C) to prevent condensation or adsorption of CAH. A two-way valve connected the helium line to the end of the GC and permitted the GC effluent to be directed either to the mass spectrometer or to a vent. A needle valve and a flow meter were fitted on the helium line and vent port of the two-way valve, respectively. This allowed us to regulate the flow of pure helium to match the flow coming from the GC during venting. This, in turn, kept the conditions in the plasma source of the mass spectrometer constant.

The flow of helium and analyte was fed to a mixing chamber, where it was entrained in an auxiliary flow of Ar before introduction to the ICP torch (Figure 1).

MC-ICPMS. The MC-ICPMS instrument is a standard Thermo Finnigan Neptune. We used an entrance slit setting of 16 μM to achieve a mass resolving power (MRP) of ~10 000 ($\text{MRP} = m/\Delta m$). The high MRP was used to resolve $^{37}\text{Cl}^+$ ($m/z = 36.96590$) from $^1\text{H}^{36}\text{Ar}^+$ ($m/z = 36.97537$).¹⁶ At an MRP of near 10 000, a small but distinct part of the mass 37 peak in the mass spectrum, at the low mass side, can be attributed solely to ^{37}Cl (Figure 2). This plateau of 0.004 amu in a total peak width of ~0.05 amu proved to be sufficiently stable to enable high precision $^{37}\text{Cl}/^{35}\text{Cl}$ ratios to be measured. Ion beams were detected using Faraday cups with amplifier resistors of $10^{11} \Omega$ for each collector.

Materials. Two different solvents were tested in this method, TCE and PCE, both of which had been analyzed extensively previously² and used as model CAH compounds to develop the method. Both solvents are free of additives and antioxidants, as is often the case in commercial CAH. Although not reported here, we have analyzed other compounds, and the method should be

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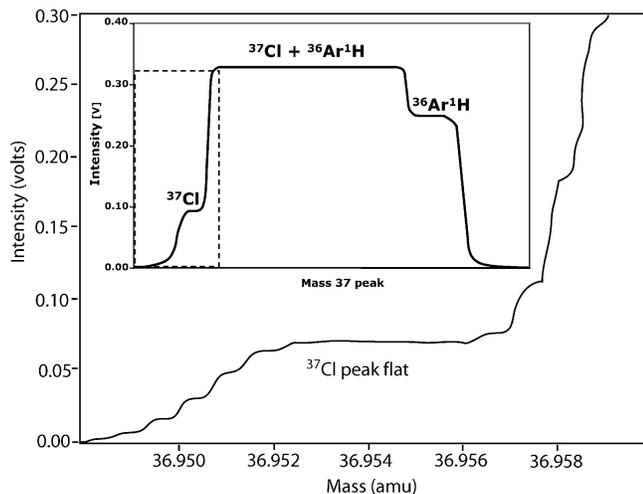


Figure 2. A single scan of the low mass edge of the mass 37 peak, with a diagram of the whole peak shown inset with exaggerated vertical scale and the area of interest identified by a dotted rectangle. The mass spectrometer was tuned to a peak center value of mass 35, but the x axis shows the measured mass values plus 2 amu to indicate the resolution on the 37 peaks.

applicable to all CAHs by adjusting the GC conditions to ensure sufficient peak resolution.

Procedure. Different amounts of the sample, ranging from 0.02 to 0.12 μL , corresponding to 200 nmol to 1.3 μmol , depending on the specific CAH, were analyzed. This is equivalent to a range of Cl from 24 to 165 μg , again depending on the CAH.

Pure TCE and PCE solvents were injected directly on the GC column, either as one solvent or as a mixture of solvents. Prior to injection, the two-way valve was put into the vent position. After 1 min, the 2-way valve was switched, connecting the GC effluent to the MC-ICPMS. One minute after switching the 2-way valve (and ~ 2.5 min after the solution was injected), the TCE peak emerged from the column, and the transient ^{37}Cl and ^{35}Cl signals were measured on the Faraday collectors of the MC-ICPMS. The background between analyte peaks showed no evidence of overlap of peak tails; backgrounds were 10^{-3} – 10^{-4} V for all runs, and the background values between analyte peaks showed no variation. PCE peaks emerged ~ 3 min after TCE at 180 $^{\circ}\text{C}$. This was the minimum separation necessary to ensure that the TCE tails did not interfere with the PCE isotope ratio measurement. Instrumental isotopic mass bias was corrected for by sample–standard comparisons using a solvent as the standard.

Transient Signal Treatment. Signal intensities from samples introduced in a MC-ICP-MS by chromatographic systems are transient, as is typical of continuous flow SIRMS. The plots of intensities of the transient signal against time are Gaussian-type curves with tails (Figure 3). Transient peaks were sampled using 0.1-s integration times throughout the duration of the peak. The stable isotope ratios are calculated by integrating both ^{35}Cl and ^{37}Cl signals and computing the ratio of the integrated data for every sample or reference.

Integration of the data was performed in Microsoft Excel after importing intensities of the transient signal from the acquisition software. To avoid mass bias, the start and end of the transient signal have to be determined carefully. Start times are easily determined as a high rate of increase of the intensity. Under our chromatographic conditions, peak tailing was significant, making

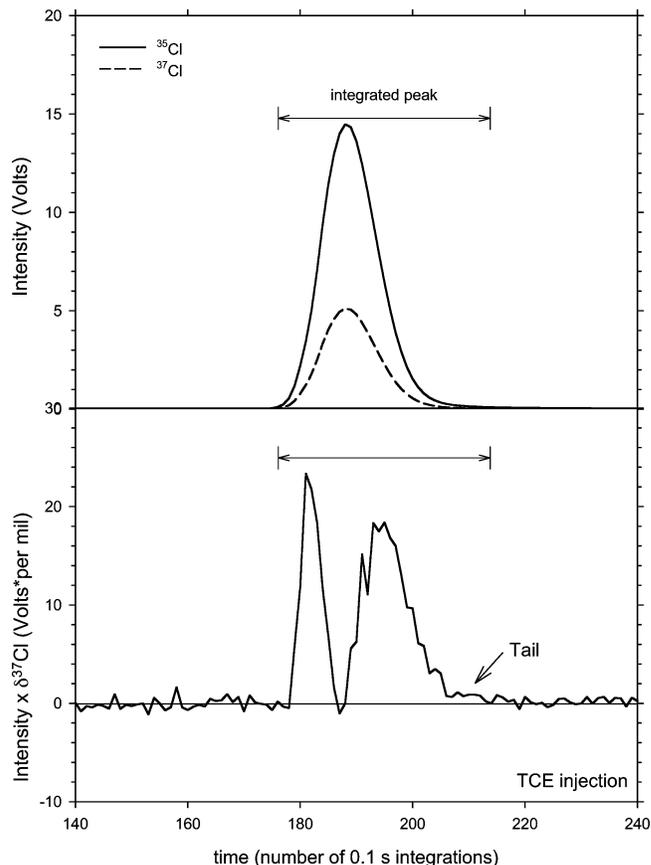


Figure 3. Typical ^{37}Cl and ^{35}Cl peaks as measured on the MC-ICPMS instrument. Upper panel shows Faraday voltage signals as a function of time for $1 \times 10^{11}\text{-}\Omega$ resistors. The time axis is in number of 0.1-s integrations. Lower panel shows the $^{37}\text{Cl}/^{35}\text{Cl}$ ratio across the peaks expressed as volts \times per mil deviations from the isotope ratio, corresponding to the time of the ^{35}Cl and ^{37}Cl peak maxima (the maxima of the two peaks are indistinguishable). The important influence of the peak “tails” is clearly visible on the isotope ratio trace.

the accurate determination of the end of the transient signal more difficult. We found accuracy and precision were maximized by retaining the entire tail of each peak until there was no discernible signal above background.

Safety Considerations. CAHs are toxic and potentially carcinogenic. Therefore, they should be handled with the appropriate precaution in well-ventilated rooms and disposed off appropriately.

RESULTS

Precision. Zero enrichment tests, in which either TCE or PCE solvent was injected as a standard followed closely in time by the same solvent sample serving as the unknown analyte, were used to investigate the reproducibility of the method. The $\delta^{37}\text{Cl}$ values were calculated from the raw data in two ways. The first determined the relative difference of the $^{37}\text{Cl}/^{35}\text{Cl}$ of each TCE injection from that ratio in the preceding one. This approach is similar to that used in some applications of continuous flow SIRMS. The other calculation is more akin to that used in dual-inlet SIRMS, in which potential drift in the signals is accommodated by comparing the ratio to the interpolated value of the preceding and subsequent measurements. This approach, like the other one, is not perfectly statistically rigorous, since each

Table 1. Zero Enrichment Values To Show Precision of TCE and PCE Analyses

sample size (μL), type	no. of analyses	$\delta^{37}\text{Cl}$ calcd rel to previous value		$\delta^{37}\text{Cl}$ calcd rel to interpolation of previous, next values	
		mean	std error	mean	std error
0.12 TCE	11	+0.02	0.15	-0.03	0.13
0.04 TCE	10	-0.05	0.21	0.00	0.14
0.02 TCE	5	-0.01	0.52	+0.18	0.56
all TCE	26	-0.01	0.14	+0.01	0.12
0.04 PCE	4	-0.17	0.18	+0.04	0.15
0.02 PCE	6	-0.04	0.33	-0.03	0.28
all PCE	10	-0.10	0.19	0.00	0.18

measurement is not completely independent of the others, and a certain amount of smoothing occurs; however, such calculations are built into the operating software of commercial mass spectrometers. We made 27 successive injections of TCE samples sized at 1.2, 0.04, and 0.02 μL and 10 successive injections of PCE (data summary in Table 1 and full data in Supporting Information, Tables S1 and S2). Analytical uncertainties are presented as standard error of the mean (σ/n^{-2}). In all cases, the mean value for each sample size was zero within the measurement uncertainties, and there were no significant differences between the two ways of calculating δ values. More importantly, there is effectively no variation in precision for either sample type for all but the smallest samples, 0.02 μL , for which the standard error increased from ≤ 0.2 to 0.3‰ for PCE and 0.5‰ for TCE.

Accuracy. Chlorine isotope values are reported relative to SMOC.⁴⁻⁶ Because seawater cannot be analyzed using our method, it was necessary to use another compound as a reference. The accuracy of the method was, therefore, tested using TCE as reference and PCE as sample. It had been shown previously that the PCE was -2.3% relative to the TCE.² We did two different types of test. In the first method, alternate injections of the TCE and PCE gave an average difference, relative to TCE, of $-2.00 \pm 0.06\%$ (1 standard error) using the GC/MC-ICPMS method (Table 2a). We were able to calculate zero enrichment values from these data and it is interesting to note that despite the greater time between analyses, the mean value is only $0.05 \pm 0.08\%$ (1 standard error). In the other method, a solution containing 50% of each pure solvent was prepared, of which 0.24 μL was injected in the GC set at a constant temperature of 160 °C. The retention times for both compounds were sufficiently different to allow separation but were similar enough to use TCE as a standard to calculate the isotopic value of the PCE. Using the full data set (Table 2b), the $\delta^{37}\text{Cl}$ of PCE was $-2.08 \pm 0.36\%$ relative to TCE (1 standard error). However, by accident, the transfer tube was not heated for the first two analyses. If these two data are eliminated, the measured difference is $-2.22 \pm 0.06\%$ (1 standard error). The results show that we can reproduce known isotopic differences within the uncertainties of the analyses.

Minimum Sample Size. We found that even at the smallest volume of CAH tested, 0.02 μL , which is ~ 200 nmol, the results were very satisfactory. The measured values were the same as for a sample of 0.12 μL to within 0.06‰; however, there is a loss of precision when the sample size is decreased below 200 nmol.

Table 2. Accuracy of Method from $\delta^{37}\text{Cl}$ Differences of TCE and PCE

	alternate injections of TCE, PCE		TCE-PCE mixture	
	TCE/TCE-1	TCE-PCE	TCE-PCE	TCE-PCE
TCE-1	0.00			
PCE-1		-1.95	-0.47	
TCE-2	-0.08			
PCE-2		-2.06	-3.03	
TCE-3	-0.14			
PCE-3		-1.97	-2.04	-2.04
TCE-4	+0.25			
PCE-4		-1.74	-2.06	-2.06
TCE-5	-0.17			
PCE-5		-2.21	-2.31	-2.31
TCE-6	-0.09			
PCE-6		-2.04	-2.05	-2.05
TCE-7				
PCE-7			-2.63	-2.63
mean	-0.05	-2.00	-2.08	-2.22
std error	0.08	0.07	0.36	0.06

DISCUSSION

Comparison with the Standard Method. The solvents used to test this method are the same as those used by Jendrzewski et al.² To check that the $\delta^{37}\text{Cl}$ (‰/SMOC) had not changed during storage through evaporation or degradation, the solvents were reanalyzed using the original method, and no differences were found. The TCE and PCE used in the accuracy tests had $\delta^{37}\text{Cl}$ (‰/SMOC) of $+2.04 \pm 0.12\%$ and $-0.30 \pm 0.14\%$.² Given these results, the $\delta^{37}\text{Cl}$ relative to TCE should be $-2.34 \pm 0.51\%$ (combined uncertainties), and the $\delta^{37}\text{Cl}$ (‰/TCE) obtained for PCE with the newly developed method is $2.22 \pm 0.06\%$. These two values are similar given the uncertainties of each result. This means that the newly developed method is at least as accurate as the previous method.

Advantages of the Method. Our newly developed method has dramatically reduced the negative impacts of the previously published methods. Complexity of preparation and analysis time have been reduced. The two-stage preparation and conversion to CH_3Cl have been eliminated. The time needed previously for a batch of eight samples (typical of a real example for analysis of two environmental water samples, each of which has four principal CAH components), including analysis of standards, would have been 12 days, during which eight person days of work were performed. This would take 2 h using our new method. Even using the newer method for converting inorganic chloride to CH_3Cl ,¹⁷ there is still a very considerable saving of time. The previous methods of chlorine isotope analysis, SIRMS and TIMS, offer sensitivities of 140 and 10 μg of Cl, respectively,⁷ and our new method can match this level. Although the precision of our approach is not quite as good as that of SIRMS, its chief benefit, the capability for rapid analysis of each CAH in multicomponent mixtures, outweighs that disadvantage. This should release the potential for Cl isotope analysis of environmental pollution samples to monitor extent and details of processes for both engineered and intrinsic remediation approaches.

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CONCLUSION

The feasibility of the approach has been proven. The analyses in which TCE and PCE were injected as a mixture have shown the possibility of including an internal standard, an approach more comparable with continuous flow isotope ratio mass spectrometry than the dual inlet approach, and should offer an explosion of use similar to that which the former has done.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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