Compound-specific hydrogen isotope analysis of fluorine-, chlorine-, bromine- and iodine-bearing organics using gas chromatography-chromium-based high-temperature conversion (Cr/HTC)-isotope ratio mass spectrometry

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ABSTRACT

RATIONAL: The conventional high-temperature conversion (HTC) approach towards hydrogen compound-specific isotope analysis (CSIA) of halogen-bearing (F, Cl, Br, I) organics suffers from incomplete H₂ yields and associated hydrogen isotope fractionation due to generation of HF, HCl, HBr, and HI byproducts. Moreover, the traditional off-line combustion of highly halogenated compounds results in incomplete recovery of water as an intermediary compound for hydrogen isotope ratio mass-spectrometry (IRMS), and hence also leads to isotope fractionation. This study presents an optimized chromium-based high-temperature conversion (Cr/HTC) approach for hydrogen CSIA of various fluorinated, chlorinated, brominated and iodinated organic compounds. The Cr/HTC approach is fast, economical, and not affected by low H₂ yields and associated isotope fractionation.

METHODS: The performance of the modified gas chromatography-chromium-based high-temperature conversion (GC-Cr/HTC) system was monitored and optimized using an ion trap MS. Quantitative conversion of organic hydrogen to H₂ analyte gas was achieved for all halogen-bearing compounds. The corresponding accuracy of CSIA was validated using (i) manual dual-inlet (DI)-IRMS after off-line conversion to H₂, and (ii) elemental analyzer (EA)-Cr/HTC-IRMS (on-line conversion).

RESULTS: The overall hydrogen isotope analysis of F-, Cl-, Br-, I-bearing organics via GC-Cr/HTC-IRMS achieved a precision σ ≤ 3 μUr and an accuracy within ±5 μUr along the VSMOW-SLAP scale compared to the measured isotope compositions resulting from both validation methods, off-line and on-line. The same analytical performance as for single-compound GC-Cr/HTC-IRMS was achieved compound-specifically for mixtures of halogenated organics following GC-separation to baseline resolution.

CONCLUSIONS: GC-Cr/HTC technology can be implemented in existing analytical equipment using commercially available materials to provide a versatile tool for hydrogen CSIA of halogenated and non-halogenated organics.

KEYWORDS: chromium, compound-specific stable isotope analysis (CSIA), fluorine-, chlorine-, bromine- and iodine-bearing organics, gas chromatography (GC), high-temperature conversion (HTC), hydrogen isotopes, isotope ratio mass spectrometry,

Introduction

Hydrogen stable isotope analysis provides a powerful tool in many disciplines, e.g. in earth sciences, ecology, forensics and biochemistry.[1] In environmental sciences, hydrogen compound-specific isotope analysis (CSIA) has evolved into a widely applied method for evaluating the origin, fate and in situ transformations of common environmental pollutants.[2] However, accurate hydrogen CSIA of halogen-bearing (i.e. F, Cl, Br, I) organics using conventional high-temperature conversion (HTC) has been long fraught with difficulties, due to the formation of H-containing byproducts HF, HCl, HBr and HI (Figure 1).[4-8] Moreover, H₂ recovery from bi- and trichlorinated ethylenes by traditional off-line combustion to water and subsequent reduction to H₂ was recently reported to be non-quantitative and affected by isotope fractionation.[9] The latter problem was less significant for organic compounds with lower atomic X/H ratios (where X = halogens), but nevertheless disqualifies off-line δ²H values of extensively halogenated compounds. The inability of traditional off-line and conventional HTC methods to quantitatively generate H₂ and accurately measure δ²H values of halogenated organic compounds prompted the development of chromium-based reactor systems that are not affected by incomplete H₂ yields and isotope fractionation. The underlying principle of chromium-HTC (Cr/HTC) applications is chrome’s ability to quantitatively scavenge carbon, nitrogen, oxygen, sulfur and halogens (F, Cl, Br, I) at elevated temperatures while quantitatively releasing H₂ into the carrier stream of an inert noble gas (Figure 1).[10-14]

Our recent study emphasized the need for thermal stability of chromium reaction products, especially chromium halide salts, for Cr/HTC’s sustainable performance.[9, 14] Chromium halides are thermally more stable than chromium carbides, nitrides, or oxides. Continued pyrolytic admission of C, N, and O into a uniformly hot reactor’s chromium filling will gradually displace halogens towards the end of the chromium filling and may eventually cause halogens to become available for hydrogen to
form HF, HCl, HBr, and HI byproducts and corrupt CSIA. This study builds on a previously described chromium-based reactor system where the GC-Cr/HTC-IRMS interface and conversion conditions have been further optimized for hydrogen CSIA of halogenated organics. $\delta^2$H values of a suite of $n$-alkanes and halogenated pure organic test compounds were further verified using either chromium-based on-line conversion combined with EA-IRMS, or off-line conversion combined with manual DI-IRMS (Table 1).\[^{14, 15}\]

**EXPERIMENTAL SECTION**

**Reference materials**

In total, twenty hetero-element (F-, Cl-, Br-, I-) bearing compounds were used, including halogenated compound classes such as benzenes, methanes, ethanes, ethenyes, and several chlorinated insecticides. Detailed information about suppliers and purities can be found in Table 1. Methyl iodide (no. #1, purity ≥99.5 %), cis-dichloroethylene (no. #2, purity ≥ 99.5 %), and trichloroethylene (TCE$_{As}$, purity ≥ 99.5 %) were provided in sealed glass ampoules from Indiana University’s array of organic stable isotope reference materials.\[^{13}\] All compounds had been previously isotopically characterized (1) on-line at the Leipzig Laboratory for Stable Isotopes (LSI) using a chromium-based EA-Cr/HTC-IRMS system, as well as in part by (2) off-line measurements at Indiana University using combustion over CuO, reduction of water to $H_2$ with uranium at 800°C, and manual DI-IRMS, as described elsewhere\[^{9, 13, 14}\]. International reference materials USGS67, USGS68, USGS69 (Reston Stable Isotope Laboratory, U.S. Geological Survey, Reston, US), as well as newly developed C$_{12}$, C$_{14}$, C$_{15}$ and C$_{17}$ $n$-alkane laboratory reference materials (≥ 99 % pure) were used for calibration and normalization along the VSMOW-SLAP isotope scale (Table 1).

**Chromium reactor assembly**

Our assembly includes a commercially available GC-HTC-IRMS interface (GC-Isolink, GC/C-III-HTC-system, Thermo Fisher, Bremen, Germany) that housed tubular ceramic reactors (320 mm, 0.8 mm i.d., 1.6 mm o.d.; Degussit AL23 aluminum oxide ceramic, Friatec, Bremen, Germany). The chromium-based reactor was assembled from a ceramic tube containing a 280-mm long chromium filling (purity > 99 %, particle size 250-300 µm, Cr Patinal®, Merck, Darmstadt, Germany) extending beyond the length of the high-temperature oven. Both ends of the bed of chromium powder were abutted by ~5-mm plugs of quartz wool (HEKAtech GmbH, Wegberg, Germany) (Figure 2). Prior to its routine use, the reactor was heated overnight to the operating temperature of about 1200°C and equilibrated with $n$-alkane reference materials until $\delta^2$H values stabilized.

**Hydrogen isotope measurements**

**Off-line analyses via uranium conversion and DI-IRMS**

The off-line conversion of organic hydrogen to water, subsequent reduction to $H_2$ with uranium metal and isotope analysis were performed at Indiana University as described by Gehre et al.\[^{9}\] In brief, organic compounds were first combusted in the presence of copper, copper (II) oxide and silver in evacuated and sealed “quartz” ampoules overnight at 800°C. Organic hydrogen was oxidized to water and subsequently reduced with uranium metal at 800°C to generate $H_2$. Hydrogen gas was collected with a teopper pump, quantified manometrically, transferred into Pyrex® glass tubes, and measured with an Delta Plus isotope-ratio mass spectrometer (Thermo Finnigan, Bremen, Germany) manually in dual-inlet mode relative to hydrogen gases prepared from VSMOW and SLAP via the uranium method.\[^{15}\]

**On-line analyses via EA-Cr/HTC-IRMS**

An HTO high-temperature conversion elemental-analyzer (HEKAtech, Wegberg, Germany) was plumbed for reversed “bottom-up” flow, equipped with a modified tube-in-tube reactor (ceramic tubes), and connected via a ConFlo IV interface to a MAT 253 isotope-ratio mass spectrometer (both from Thermo Fisher Scientific, Bremen, Germany).\[^{16}\] EA-Cr/HTC-IRMS measurements were performed as described by Gehre et al.\[^{9}\] using a conversion temperature of 1200-1250°C. Analyses of pure compounds were performed in triplicate, and resulting raw data were normalized via 2-point calibration along the VSMOW-SLAP isotope scale as described below.

**On-line analyses via GC-Cr/HTC-IRMS**

Analyses via GC-Cr/HTC-IRMS utilized an analytical train featuring a CTC CombiPAL auto-sampler (CTC Analytics AG, Zwingen, Switzerland), a GC (HP7890, Agilent Technologies, Ratingen, Germany), and a GC IsoLink interface connected via ConFlo IV open split system to a MAT 253 IRMS (all from Thermo Scientific, Bremen, Germany). The gas chromatograph was equipped with a Zebron ZB-1 column (60 m, 0.32 mm i.d., 1 µm thin film thickness; Phenomenex Inc., Torrance, USA). Samples in solution were introduced via split/splitless injection in amounts that represented the hydrogen equivalent of ~80-100 nmol H passing onto the column from each compound. Cr/HTC and resulting compound-specific hydrogen isotope compositions were investigated at conversion temperatures of 1200°C and a post-reactor helium carrier gas flow of 1.4 mL min$^{-1}$. $H_2$ was transferred on-line through an open split into the isotope-ratio mass spectrometer. The $H_3^+$ factor was measured twice daily.

**Analysis of byproducts**

The formation of byproducts during Cr/HTC was monitored with a PolarisQ ion trap mass spectrometer (Thermo Finnigan, Bremen, Germany) coupled to a gas chromatograph (HP6890N, Agilent Technologies, Ratingen, Germany, with auto-sampler A200S, CTC Analytics AG, Zwingen, Switzerland) that was...
Normalization of isotope values

Normalization of raw δH values along the VSMOW-SLAP scale relied on routine 2-point calibration with GC-compatible n-hexadecanes USGS67 and USGS69. All GC-derived data were thus uniformly normalized to compensate for scale compression of the mass spectrometer and to arrive at corrected δH values along the VSMOW-SLAP isotopic scale. Additional laboratory reference material for quality control were n-hexadecane USGS68, as well as C12, C14, C15 and C17 n-alkanes (≥ 99 % pure) that had been calibrated at the UFZ Leipzig via EA-Cr/HTC-IRMS. It is important to note that so-called ‘reference gas pulses’ of hydrogen in the carrier gas stream do not perform well in Cr/HTC, as discussed elsewhere. More importantly, the principle of identical treatment of sample and standard mandates that the chemical nature of the standards and their passing through the analytical train are closely comparable to those of the samples. An injected ‘H2 reference gas’ pulse cannot serve as a substitute for organic reference materials.

The abundance ratio of hydrogen isotopes $^{2}\text{H}/\text{H}$ is expressed in customary δ notation [Eq. 1]. In contrast to traditionally applied per mil (‰), all values are reported in the SI unit urey (here mUr, which is equivalent to ‰) following the recommendation of Brand and Coplen.[21]

$$\delta^{2}\text{H}[\text{mUr}] = (R_{\text{Sample}} / R_{\text{Reference}} - 1)$$  \[1\]

RESULTS AND DISCUSSION

Principles

Chromium-based HTC reactor systems provide an elegant solution for hydrogen isotope analysis of nitrogen-bearing compounds. In contrast to stable chromium nitride, however, the limited thermal stability of chromium halides requires additional optimization of the Cr/HTC reactor design towards permanent capture of halogens by the chromium packing. The captured chromium halides within GC-Cr/HTC reactors were found at the back end of the chromium filling in a region of lower temperatures, indicating that colder reactor regions are required for stable chromium-halides formation and deposition (Figure 2), similar to our previous observations for EA-Cr/HTC.[9] The optimized reactor design therefore utilizes a decreased peak conversion temperature of 1200 °C and extends the chromium filling beyond the end of the furnace to provide a lower range of temperatures where all chromium halides are thermally stable.

Byproduct formation from halogen-bearing compounds

The conversion efficiency of halogen-bearing compounds was compared between conventional GC-HTC (GC flow 1.2 mL min$^{-1}$, reactor temperature 1400 °C, empty Al$_2$O$_3$-tube) and the optimized GC-Cr/HTC (GC flow 1.2 mL min$^{-1}$, reactor temperature 1200 °C, chromium filled reactor) using equal amounts of analytes on columns (Figure 3 A-D).

The molecular background scan after HTC revealed considerable formation of H-bearing byproducts from all halogen-bearing compounds, confirming earlier observations.[6] In general, hydrogen halides were the most abundant byproducts, followed by various hydrocarbons (Figure 3 A-D).

Remarkably, the pyrolysis of fluorine-bearing compounds ultimately generated significant amounts of silicon tetrafluoride (SiF$_4$), most probably due to the reaction of HF with quartz wool or silica tubing (Figure 3 A-D).

Cr/HTC resulted in a significant reduction or absence of byproducts when compared to conventional HTC (Figure 3 A-D). Signal intensities of HX byproducts were in the range of the air/water background for all heteroatom-bearing compounds tested. Interestingly, Cr/HTC also generated some silicon tetrafluoride from fluorine-bearing compounds (Figure 3 A-D). However, silicon tetrafluoride is hydrogen-free and was not observed to affect H$_2$-yields and hydrogen isotope measurements. Long-term effects of silicon tetrafluoride on analytical equipment need to be investigated in future studies.

Hydrogen isotope analysis

Hydrogen CSIA of several n-alkanes and various halogen-bearing compounds (Table 1) with GC-Cr/HTC-IRMS achieved good precision and accuracy for almost all tested compounds. Robust precision of $\sigma \leq 3$ mUr (n ≥ 30) was achieved with good accuracy for n-alkanes (Table 1). Among halogen-bearing compounds, a typical precision of $\sigma \leq 2$ mUr (n ≥ 4) was achieved within a sequence run. The corresponding accuracy was generally within ±5 mUr based on both validation methods. For di- and tri-chlorinated ethenes (DCE, TCE), however, an offset was confirmed between the off-line conversion technique (DI-IRMS) and both on-line techniques (EA- and GC-Cr/HTC-IRMS) as a result of incomplete off-line H$_2$ yields.[14]

Compound-specific analyses of mixtures

As presented in Figure 4 and in the supporting information, a mixture of F-, Cl-, Br-, and I-benzene can be gas chromatographically separated to baseline resolution and compound-specifically analyzed. The resulting calibrated δH values of all four compounds were in good agreement with δH values of the respective pure compounds, which had been determined via EA-Cr/HTC-IRMS as well as GC-Cr/HTC-IRMS (Table 1). Peak broadening was stated in our previous report to be a critical issue for compound-specific analysis via GC-Cr/HTC.[14] Peak widths were observed to increase proportionally to rising reactor temperature due to thermal diffusion within the hot chromium filling. Consequently, high temperatures may thwart compound-specific CSIA of complex mixtures by preventing baseline resolution, accurate peak area-integration, and background correction during δH measurements of individual, insufficiently resolved GC peaks.

For this reason, the Cr/HTC reactor temperature was decreased from a previous maximum of 1400 °C to 1200 °C. The modified temperature profile still quantitatively converted all tested compound classes while affording a significant reduction in peak width. A further improvement in peak width may be possible by increasing the GC helium flow and/or using a larger chromium particle size. Further optimization, however, must not compromise the quantitative conversion of organic hydrogen from different compound classes to H$_2$. 
Figure 2: Schematic design and temperature profile of a Cr/HTC reactor positioned within a standard HTC-furnace (not true to scale). Hetero-elements, such as oxygen, nitrogen and halogens are irreversibly scavenged by chromium, while H$_2$ is passed through as analyte gas for $\Delta^2$H determination. Chromium reaction products (Cr-carbide, -oxide, -nitride and -halides) deposit along the thermal gradient of the chromium-filled packing in appropriate temperature intervals. The lower-temperature tail end of the chromium bed is necessary to guarantee immobilization and thermal stability of chromium halides.

Figure 3: The ion trap mass spectrometer monitored the formation of byproducts during HTC (red) versus Cr/HTC (blue) of (A) fluorobenzene, (B) chlorobenzene, (C) bromobenzene and (D) iodobenzene. HTC resulted in formation of hydrogen halides (HX), while Cr/HTC produced non-detectable or limited amounts of byproducts.
Table 1: $\delta^2$H values for $n$-alkane and diverse halogen-bearing reference materials determined and evaluated using off-line DI-IRMS, on-line EA-Cr/HTC-IRMS and on-line GC-Cr/HTC-IRMS. All $\delta^2$H values have been normalized to the VSMOW-SLAP scale using 2-point calibration and are expressed in the SI unit urem (mUr, equivalent to ‰).

* GC-compatible reference material used for 2-point calibration along the VSMOW-SLAP isotopic scale; n.d. – not determined; n.a. – not available; IU – provided by Indiana University.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Supplier</th>
<th>Purity [%]</th>
<th>Formula</th>
<th>$\delta^2$H reference value [mUr]</th>
<th>$\delta^2$H off-line DI-IRMS [mUr]</th>
<th>$\delta^2$H on-line EA-Cr/HTC-IRMS [mUr]</th>
<th>$\delta^2$H on-line GC-Cr/HTC-IRMS [mUr]</th>
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<td>-168.1 (30)</td>
<td>-166 ± 3 (30)*</td>
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<td>-11.0 (24)</td>
<td>-10.6 ± 2 (30)</td>
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<td>+373.6 (9)</td>
<td>+386.9 (20)</td>
<td>+381 ± 3 (30)*</td>
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<td>-188 ± 2 (30)</td>
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<td>-68 ± 3 (30)</td>
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<td>+73 ± 2 (11)</td>
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Figure 4: Hydrogen isotope data in the form of a CSIA trace (m/z = 2 and 3) of a GC-resolved mixture containing F-, Cl-, Br- and I-benzene via GC-Cr/HTC (orange) are compared with data from single compounds via EA-Cr/HTC (blue) and GC-Cr/HTC (red). The δH values of the measured compounds cover a range of -335 to +40 mUr (ΔδH ~ 375 mUr).

Figure 5: Memory test during compound-specific hydrogen isotope analysis. A mixture of halogen-bearing (F-, Cl-, Br-, I-) benzenes was measured five times via GC-Cr/HTC-IRMS. All values were 2-point calibrated along the VSMOW-SLAP scale using n-hexadecanes USGS67 and USGS69. Dashed lines represent the corresponding δH-values determined via EA-Cr/HTC-IRMS.

Memory
Memory effects in mixed samples were evaluated using a mixture containing F-, Cl-, Br- and I-benzene (Figures 4 and 5). Remarkable stability persisted throughout the analyses of various halo-benzenes spanning a Δ380 mUr wide isotopic range from -335 to +42 mUr. Minor memory effects were observed during compound-specific analyses of a mixture. Sufficient peak separation is therefore mandatory to avoid background interferences during isotope analysis.

Equilibration and linearity
Chromium-based reactor systems usually require longer conditioning and equilibration time compared to conventional oxidation and pyrolysis reactors. Therefore, stability and linearity should be evaluated with appropriate reference materials prior to measurements of unknown samples. A routine 2-point calibration with organic reference materials compensates for variability in machine slope and is therefore mandatory for accurate hydrogen isotope measurements. A non-linear shift of δH-values was observed below an m/z = 2 signal amplitude of 4000 mV for all compounds, while linearity was generally satisfying above 4000 mV (Figure 6). A similar non-linear shift was measured for pure H2 gas pulses of different sizes that were manually injected into the head space above the GC column in both Cr/HTC and conventional HTC setups, indicating that chromium-based conversion is not the cause for the observed linearity issue (Figure 6). Aluminum oxide ceramics are currently suspected to become partially permeable for molecular hydrogen at high temperature, which can potentially lead to fractionation and isotopic offset at low signal amplitudes. Our current GC-Cr/HTC-IRMS system has a practical lower sample size limit of about 80 nmol H on column generating a signal amplitude of at least 4000 mV.

CONCLUSIONS
Chromium-based reactor systems are a versatile and promising extension for compound-specific hydrogen isotope analysis of hetero-element bearing compound classes and are especially advantageous for analyses of anthropogenic compounds with environmental significance. Our optimized GC-Cr/HTC application especially targets a broad range of halogen-bearing compounds for which accurate on-line determinations of δH values was not possible with the conventional HTC approach. In addition, the improved chromium-based approach may offer access to compound-specific hydrogen isotope analysis of polar
organics using derivatization methods that introduce halogens but no new hydrogen. In general, chromium-based reactors are as simple to use as conventional HTC/pyrolysis reactors, and may, therefore, provide a universal tool for routine hydrogen isotope analysis of halogen-bearing and halogen-free organics.

Figure 6: Linearity of $\delta^2$H values across increasing sample size for (A) $H_2$ gas pulses injected into HTC versus Cr/HTC setups; (B) various n-alkanes (C$_{12}$, C$_{14}$, C$_{15}$, C$_{16}$ and C$_{17}$) and (C) halogenated benzenes (F-, Cl-, Br- and I-benzene) after Cr/HTC. A non-linear shift was observed at m/z = 2 signal amplitudes below 4000 mV for all compound classes and reactor types. Dashed lines represent the corresponding $\delta^2$H values determined via EA-Cr/HTC-IRMS.

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Notes
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REFERENCES


