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# Optimization of on-line hydrogen stable isotope-ratio measurements of halogen- and sulfur-bearing organic compounds using elemental analyzer-chromium/high-temperature conversion-isotope-ratio mass spectrometry (EA–Cr/HTC–IRMS)

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**RATIONALE:** Accurate hydrogen isotopic analysis of halogen- and sulfur-bearing organics has not been possible with traditional high-temperature conversion (HTC) because the formation of hydrogen-bearing reaction products other than molecular hydrogen ($H_2$) is responsible for non-quantitative $H_2$-yields and possible hydrogen isotopic fractionation. Our previously introduced, new chromium-based EA-Cr/HTC-IRMS (Elemental Analyzer – Chromium/High Temperature Conversion – Isotope-Ratio Mass Spectrometry) technique focused primarily on nitrogen-bearing compounds. Several technical and analytical issues concerning halogen- and sulfur-bearing samples, however, remained unresolved and required further refinement of the reactor systems.

**METHODS:** The EA-Cr/HTC reactor was substantially modified for the conversion of halogen- and sulfur-bearing samples. The performance of the novel conversion setup for solid and liquid samples was monitored and optimized using a simultaneously operating dual-detection system of IRMS and ion trap MS. The method with several variants in the reactor, including the addition of manganese metal chips, was evaluated in three laboratories using EA-Cr/HTC-IRMS (on-line method) and compared with traditional uranium-reduction-based conversion combined with manual dual-inlet IRMS analysis (off-line method) in one laboratory.

**RESULTS:** The modified EA-Cr/HTC reactor setup showed an overall $H_2$-recovery of more than 96 % for all halogen- and sulfur-bearing organic compounds. All results were successfully normalized *via* 2-point calibration with VSMOW-SLAP reference waters. Precise and accurate hydrogen isotopic analysis was achieved for a variety of organics containing F-, Cl-, Br-, I-, and S-bearing heteroelements. The robust nature of the on-line EA-Cr/HTC technique was demonstrated by a series of 196 consecutive measurements with a single reactor filling.

**CONCLUSIONS:** The optimized EA-Cr/HTC reactor design can be implemented in existing analytical equipment using commercially available material and is universally applicable for both heteroelement-bearing and heteroelement-free organic-compound classes. The sensitivity and simplicity of the on-line EA-Cr/HTC-IRMS technique provide a much needed tool for routine hydrogen-isotope source tracing of organic contaminants in the environment.

KEYWORDS: halogenated hydrocarbons, environmental tracing, high-temperature chromium reduction, hydrogen stable isotopes, on-line isotope ratio mass spectrometry, organic sulfur, pyrolysis

## INTRODUCTION

Natural and anthropogenic heteroelement-bearing organic compounds are commonly encountered in the biosphere and atmosphere, and more specifically in critical natural environments such as soils, surface waters, and groundwaters. Analytical urgency derives from the need for forensic characterization of environmental pollutions and of industrial contaminants in food and explosives. Multidimensional stable isotopic analysis of hydrogen, carbon, sulfur, and chlorine provides powerful diagnostic tools to trace or constrain the origin, transport, and partial degradation of materials on a compound-specific level.[1]

Accurate hydrogen isotopic analysis *via* isotope-ratio mass spectrometry (IRMS) requires elemental $H_2$ that needs to be produced quantitatively from an analyte in order to avoid isotopic fractionation. Chromium-based techniques were first applied for the conversion of water to hydrogen gas.[2, 3] For halogenated organic compounds pyrolytic liberation of $H_2$ in the presence of hot chromium was first described in pioneering articles by Armbruster *et al.* [4] and Vetter *et al.* [5] However, the previously applied chromium reactor design and the prescribed conversion temperature of 1050 °C generated inconsistent $H_2$-yields. Furthermore, the measured $\delta^2$H values could not be properly calibrated in the absence of suitable hydrogen stable isotopic reference materials.

Our recent introduction of a chromium-based elemental analyzer (Cr-EA) connected on-line to IRMS instrumentation was primarily developed and evaluated for nitrogen-bearing organic compounds.[6-8] This article describes a modified and improved EA-Cr/HTC reactor operating at higher temperatures. The following issues were addressed:

(i) quantitative and irreversible conversion of organic hydrogen from halogen- (X = F, Cl, Br or I) and sulfur-bearing compounds to $H_2$ by high-temperature reactions of the halogens with chromium to $CrX_3$ and $Cr_2S_3$ or manganese to $MnX_2$ and MnS, respectively;
(ii) unrestricted utilization of stable isotopic reference waters interspersed with analysis of halogen- and sulfur-bearing organic analytes;
(iii) extended chromium reactor life time and stability of hydrogen conversion;
(iv) application of the EA-Cr/HTC reactor for solid and liquid analytes.

Our optimized EA-Cr/HTC-IRMS technique offers a significant extension of hydrogen isotopic analysis of F-, Cl-, Br-, I-, and S-bearing substances. Quantitative on-line conversion of organic hydrogen to $H_2$ was performed and accurate $\delta^2$H values were determined on all analyzed compounds. The $\delta^2$H values were verified using either chromium-based on-line conversion, combined with EA-IRMS, or off-line conversion, combined with manual dual-inlet isotope-ratio mass spectrometry (DI-IRMS).[9] The evaluated reactor variants can be implemented in existing analytical equipment by replacing the EA-HTC (also known as TC/EA for temperature conversion/elemental analysis, ThermoFinnigan, Bremen, Germany) with a Cr (or Cr/Mn) reactor (i.e. any Elemental Analyzer operating up to 1300 °C, TC/EA) using commercially available materials.

## EXPERIMENTAL

### Reference materials and chemicals

Internationally distributed isotopic reference waters VSMOW, VSMOW2, SLAP, SLAP2 and GISP were used for normalization of the VSMOW-SLAP isotope-delta scales. In addition, $^2$H-enriched reference waters IAEA-604[10], UC04 and USGS W-89262, as well as polyethylene IAEA-CH-7, were used for validation. Chemicals such as iodomethane, cis-dichloroethylene, and trichloroethylene were provided in sealed glass ampoules from stocks at Indiana University (Bloomington, IN, USA).[7] Several halogen- and sulfur-bearing substances were described by Renpenning *et al.* [11] including p,p'-dichlorodiphenyl dichloroethane (DDD), p,p'-dichlorodiphenyldichloroethylene (DDE), 4,4'-dichlorodiphenyltrichloroethane (DDT), γ-hexachlorocyclohexane (γ-HCH), dimethyl sulfone ($DMSO_2$), diphenyl disulfide ($Ph_2S_2$), trichloroethene ($TCE_{UFZ7}$), and trichloroethene ($TCE_{UFZ8}$). Compounds analyzed also included fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, thiophene, 1,2-dibromoethane, and dimethyl disulfide. Details can be found in Table 2 and Table S-5 (Supplementary Information).

## Hydrogen isotopic analysis

In this study, relative hydrogen isotope ratios, $\delta^2$H values, are defined by the relation

$$\delta^2\mathrm{H} = \frac{R\left({}^2\mathrm{H}/{}^1\mathrm{H}\right)_\mathrm{P} - R\left({}^2\mathrm{H}/{}^1\mathrm{H}\right)_\mathrm{VSMOW}}{R\left({}^2\mathrm{H}/{}^1\mathrm{H}\right)_\mathrm{VSMOW}} \qquad [1]$$

where $R(^2\mathrm{H}/^1\mathrm{H})_\mathrm{P}$ is the ratio $N(^2\mathrm{H})_\mathrm{P}$ / $N(^1\mathrm{H})_\mathrm{P}$. $N(^2\mathrm{H})_\mathrm{P}$ and $N(^1\mathrm{H})_\mathrm{P}$ are the numbers of the two isotopes of hydrogen, $^2$H and $^1$H, respectively, in a sample P. Similarly, $R(^2\mathrm{H}/^1\mathrm{H})_\mathrm{VSMOW}$ is the international isotopic measurement standard Vienna Standard Mean Ocean Water or VSMOW.[12] The International Union of Pure and Applied Chemistry (IUPAC) recommends that use of the per mil (symbol ‰) be avoided.[13] Therefore, we follow the suggestion of Brand and Coplen [14], and we use the term urey (symbol Ur), which is suited for diverse isotope scales of all elements. One milliurey = 0.001 = 1 ‰. A delta value in the traditional form of –25 ‰ can be expressed as –25 mUr.

Analytes were characterized independently by four laboratories (off-line techniques in one laboratory and on-line techniques in three laboratories), namely (i) at Indiana University *via* off-line oxidation of organic hydrogen to $H_2O$ and uranium-based reduction to $H_2$ combined with DI-IRMS measurements, (ii) in the Laboratory for Stable Isotopes (LSI) in the Helmholtz Centre for Environmental Research (Leipzig, Germany) *via* on-line conversion using EA-Cr/HTC-IRMS and EA-HTC-IRMS, (iii) in the stable isotope laboratory (BGC-IsoLab) at the Max-Planck-Institute (Jena, Germany) using a different reactor variant of on-line EA-Cr/HTC-IRMS, and (iv) in the Reston Stable Isotope Laboratory (RSIL) at the U.S. Geological Survey (Reston, VA, USA) *via* on-line conversion using EA-Cr/HTC-IRMS.

### *Off-line combustion and reduction to $H_2$ with uranium at Indiana University*

The traditional off-line uranium-based method of hydrogen isotopic analysis first combusted organic compounds in the presence of copper and silver metals and copper (II) oxide in evacuated and sealed "quartz" ampoules overnight at 800 °C. Halogens and sulfur were quantitatively scavenged as copper halides and sulfate upon cooling to 200 °C, whereas all organic hydrogen was oxidized to water.[15, 16] Volatile reaction products were released from each freshly combusted ampoule at 200 °C and admitted into a vacuum line where $H_2O$ was cryogenically separated and subsequently reacted with uranium metal at 800 °C to quantitatively generate $H_2$. A Toepler pump transferred $H_2$ into Pyrex tubes that were sealed off. At a later date the tubes were opened, transferring $H_2$ into the manual dual-inlet system of an isotope-ratio mass spectrometer. International reference waters processed with uranium were used for 2-point normalization against the VSMOW-SLAP scale. The normalization was verified by employing $H_2$ from numerous accessory organic and water reference materials that had been processed with uranium to satisfy the principle of identical treatment (IT principle) of sample and reference material.[9, 17, 18]

### *On-line conversion via EA-Cr/HTC at LSI, Leipzig*

A HTO high-temperature conversion elemental-analyzer (HEKAtech GmbH, Wegberg, Germany) was plumbed for reversed “bottom-up” flow, equipped with a modified tube-in-tube reactor (inner tube: ceramic or quartz), and connected *via* a ConFlo IV interface to a MAT 253 isotope-ratio mass spectrometer (both from Thermo Fisher Scientific, Bremen, Germany).[19] Solid analytes were weighed into silver capsules, whereas some liquids were crimp-sealed into segments of silver tubes and analyzed as solid samples.[20] Samples were loaded into the carousel of a AS200 autosampler (Thermo Fisher Scientific) attached to the EA. The operation temperature for the EA-Cr/HTC was set to 1250 °C. For liquid injection, aliquots of 0.5–1.0 µL were loaded into a syringe and injected through a septum using an A200S liquid autosampler (CTC Analytics AG, Wengen, Switzerland). The injector temperature of 180–200 °C limited the liquid analytes to compounds with lower boiling temperatures.

The basic design of the EA-Cr/HTC reactor was previously described by Gehre *et al.* [7], but it required significant modification for hydrogen isotopic analysis of halogen- and sulfur-bearing organics (Fig. 1). The tube-in-tube reactor utilizes thermally stable $Al_2O_3$-ceramics for its outer (OD is 19 mm; ID is 15 mm; HEKAtech GmbH) and inner tubes (OD is 13 mm; ID is 9 mm; $Al_2O_3$; Friatec AG, Mannheim, Germany). From bottom to top, the inner reactor tube was loaded first with 10 mm of silver or quartz wool, followed by a layer of chromium granules (1–3-mm diameter, purity ≥99 %, ChemPUR, Karlsruhe, Germany) up to the middle of the hottest zone (for solid injection setup, temperature 1250 °C) or 4–5 cm above (for liquid injection setup). The solid injection setup also contained a graphite crucible (height is 25 mm; OD is 8 mm; ID is 6 mm) on top of the chromium filling to collect silver and other debris. The length of the chromium package needs to encompass a temperature gradient for efficient trapping of chromium salts.

*On-line conversion via EA-Cr/HTC at BGC-ISOLAB, Jena*

The experimental setup used at the Jena BGC IsoLab for solid sample HT conversion has been described in detail by Brand *et al.* [21] In brief, a HTC elemental analyzer (HTO, HEKAtech GmbH) equipped with a Zero-Blank 50-position autosampler (Costech, Pioltello, Italy) was coupled to a Delta$^{plus}$ XL isotope-ratio mass spectrometer *via* a ConFlo II open-split interface (both from Thermo Fisher Scientific). The reactor was a SiC outer tube and a glassy carbon inner tube in a tube-in-tube arrangement with reversed helium carrier gas flow.[22] The inner glassy carbon tube was usually filled with glassy carbon chips (2–3 mm in diameter) from the center of the hottest zone. In order to reduce hydrogen halide gases formed during the conversion at ~1430 °C and form $H_2$ again, we mixed the glassy carbon chips 1:1 with either chromium chips with high purity or additional manganese metal chips of the same size in the lower portion of the reactor filling.

For liquid samples, the setup was changed to a Thermo Fisher Scientific TC/EA HTC unit, connected to the same IRMS instrument and a ConFlo III interface (Thermo Fisher Scientific). In this case, the reactor tube was made from $Al_2O_3$ with a similar tube-in-tube arrangement and reactor packing. Samples were directly injected *via* a silicone septum (>130 °C) and compared directly with reference waters injected *via* the same septum. Care was taken to inject the amounts of sample in such a way as to arrive at similar peak heights and shapes for all materials.

*On-line conversion via EA-Cr/HTC at RSIL, Reston*

At the RSIL, the $\delta^2$H measurements were made using an EA-HTC-IRMS reduction unit equipped with a Costech (Valencia, CA, USA) Zero-Blank 100-position autosampler, a ConFlo IV gas introduction system, and Delta$^{plus}$ XP isotope-ratio mass spectrometer (Thermo Fisher Scientific). The glassy carbon tube inside the ceramic tube, normally filled with glassy carbon chips, was packed with chromium chips and a glassy carbon chips mixture. The mix ratio of chromium to glassy carbon chips was about 1:1. The bottom 35 mm of the ceramic tube was filled with chromium and glassy carbon chips and supported by silver wool. The helium carrier gas (100 mL/min) was fed from the top, as originally supplied. The reactor temperature was set at 1250 °C and the GC temperature was maintained at 80 °C. Solid samples were weighed into silver capsules, whereas organic liquids and reference waters were crimp-sealed into segments of silver tubes and analyzed as solid samples.[20]

*Mass-spectrometric analysis of by-products*

At the LSI, Leipzig, the formation of by-products from EA-HTC and EA-Cr/HTC conversions was monitored with a Polaris*Q* ion trap mass spectrometer (Thermo Fisher Scientific) coupled in parallel to a HTC elemental-analyzer (HTO, HEKAtech GmbH).[22] This allowed the simultaneous identification of hydrogen-containing by-products from high-temperature conversions and hydrogen isotopes, as described previously.[7, 11]

*Normalization of hydrogen stable isotope values*

Our former setup, which restricted the calibration with reference waters in combination with halogen-bearing organics, had to be revised for the modified EA-Cr/HTC reactor design. Stable isotope data were normalized at LSI in Leipzig *via* 2-point calibrations along the VSMOW-SLAP isotopic scale using VSMOW ($\delta^2$H = 0 mUr) or VSMOW2 ($\delta^2$H = 0 mUr), and SLAP ($\delta^2$H = −428 mUr) or SLAP2 ($\delta^2$H = −427.5 mUr) reference waters directly and interspersed within sample sequences. Normalization in the BGC-ISOLAB, Jena, relied on in-house reference waters that had been calibrated to the VSMOW scale ("WWW-J1" at –67.0 ± 0.5 mUr and "BGP-J1" at −187.1 ± 0.7 mUr). In the case of solid samples, in-house reference materials Pet-J1 (polyethylene powder; −78.2 ± 0.4 mUr) and Jena-Pristane (Pristane; −362.6 ± 0.5 mUr) were used. For $^2$H-enriched samples such as TCE, a $^2$H-enriched reference water USGS W-89262 ($\delta^2$H = +2555 ± 6 mUr) was used for additional control along the VSMOW-SLAP scale. Hydrogen isotope data were normalized at RSIL *via* 2-point calibrations against UC04 ($\delta^2$H = +113.6 mUr) and IAEA-604 ($\delta^2$H = +799.9 mUr)[8] on VSMOW-SLAP scale.

## RESULTS AND DISCUSSION

### Principles

Quantitative conversion of organic hydrogen to the $H_2$ analyte gas and avoidance of H-bearing by-products are essential for the determination of accurate $\delta^2$H values that reflect the total hydrogen isotopic composition in the sample. The fundamental reaction mechanisms of the EA-Cr/HTC technique are (i) the pyrolytic decomposition of organic analytes in the presence of chromium resulting in the reduction of organic hydrogen to $H_2$ at the expense of chromium being converted to stable oxide, carbide, and nitride, and (ii) the simultaneous formation of chromium halides and/or sulfides to prevent the formation of hydrogen halides and hydrogen sulfide by-products (Fig. 2). Although chromium oxides and nitrides are thermally stable and immobile at temperatures as high as 1500 °C and chromium sulfides are stable and immobile at temperatures in the range of or even below 1350 °C, the stability of chromium halides is restricted to temperatures far below 1000 °C. Thus, chromium halides appear to possess limited thermal stabilities that have to be taken into account in the EA-Cr/HTC reactor design. Contrary to the conclusions in our previous report,[7] chromium halides obviously are deposited in relatively cool sections towards the exit of the EA-Cr/HTC reactor at temperatures as low as ~200 °C. Different types of elemental analyzers and their reactors seem to require a detailed knowledge of the temperature profiles and a corresponding adaptation of the chromium packaging.

**Reactor design** The evaluation and optimization of the reactor design, by-product formation, recovery of hydrogen during conversion, stability of sequential on-line measurements and hydrogen-isotope memory effects in EA-Cr/HTC are mainly based on the system designed at LSI Leipzig (Fig. 1-A). To test the robustness of the system designed by LSI, Leipzig, the BGC-ISOLAB, Jena and RSIL USGS, Reston adopted the basic idea and came up with slightly different reactor designs (Figure 1-B/C, Table 2).

### *EA-Cr/HTC reactor setup*

Improvement of reactor performance and $H_2$ yield from EA-Cr/HTC conversion of halogen- and sulfur-bearing organic compounds required several modifications of the reactor design (Table 1, Fig. 1). Although a tube-in-tube construction using the carrier He-gas from the top and a reverse flow reactor design is presented in this study, an alternative EA-Cr/HTC setup with a single tube was also successfully implemented. The advantage was a higher sample capacity, with the disadvantage of a broader peak shape (results not shown). The EA-Cr/HTC approach can be adapted for various setups and analytical hardware.

### *Reactor material*

For the EA-Cr/HTC reactor setup we prefer the tube-in-tube construction.[19] The outer tube was made from $Al_2O_3$ ceramic and sealed the system from the atmosphere. The inner tube in the bottom up setup was preferably made from ceramic, but quartz or glassy carbon tubes were also used. However, the high costs and fragility of glassy carbon tube in combination with chromium chips (or powder) may restrict applications. Similarly, the structural integrity of quartz reactors for EA-Cr/HTC was poor, and they suffered damage above ~1250 °C and allowed only a single use. Re-usable $Al_2O_3$ ceramics, however, provided both higher thermal tolerance and structural stability up to 1900 °C.

### *Temperature gradient*

A significant modification of the EA-Cr/HTC reactor was the extension of the filling of chromium beyond the furnace at the bottom end of the reactor. Tests with different F-, Cl-, Br-, I- and S-bearing compounds demonstrated that this modification not only immobilized chromium halides within the reactor package, but also allowed accurate measurements of reference waters for normalization of the VSMOW-SLAP scale with high precision (see Table S-4, Supplementary Information). A similar effect was observed using manganese chips in the lower part of the reactor, as was tested in the BGC-ISOLAB, Jena. Any formation of HX acid during or after the initial reduction results in the formation of $MnX_2$ and gaseous $H_2$, which is added back to the $H_2$ inventory and results in stoichiometric $H_2$ yields.

### *Particle size of chromium*

Our previous reactor design used Cr-powder with a particle size of < 0.3 mm that tended to block the flow of helium after 50–100 analyses due to the deposition of elemental carbon and ash, and also as a consequence of the gradual accumulation of chromium halides. The use of coarser chromium particles with 1–3-mm diameter prevented the blocking of the carrier gas flow, while not negatively affecting the chemical conversion efficiency.

*Graphite crucibles*

The use of a graphite crucible on top of the chromium is useful not only for trapping of silver and ash, but also for collecting some of the elemental carbon that forms as a by-product of pyrolysis in the upper part of the reactor. The graphite crucible not only mitigates blocking of the carrier gas flow, but it also prevents the coating and inactivation of chromium with molten silver, which resulted in reduced $H_2$ yields and caused isotopic fractionation in our experiments (results not shown). Customized graphite crucibles at LSI in Leipzig come in two sizes, namely a narrow one for the tube-in-tube system (height is 25 mm; OD is 8 mm; ID is 6 mm) and a wider size for the single-tube system (height is 25 mm; OD is 12 mm; ID 10 mm). A crucible in the latter system can collect up to 4 g of debris from the analysis of ~200 samples representing ~70 mg of organic analyte.

## By-product formation and recovery of hydrogen during conversion

### *Off-line conversion of organic hydrogen to $H_2$*

In contrast to $H_2$ yields from water amounting to ~ 100 % of theory, the $H_2$ yields from *cis*-dichloroethene and trichloroethene were only 82 and 78 %, respectively (all experiments were performed in triplicate with a precision of ≤ 2 %). The $H_2$ yield therefore decreased with increasing Cl/H molar ratio of the analyte. The incomplete $H_2$ yields entailed isotopic fractionation by tens of milliureys in terms of artificially increased $\delta^2$H values (Table 2). Light-brown copper (II) chloride droplets condensed in the upper parts of quartz combustion ampoules upon cooling and probably held the missing hydrogen in the form of a partial hydrate and/or HCl – $CuCl_2$ adduct when volatiles were transferred at ~200 °C from combustion ampoules into the vacuum line.

### *EA-HTC*

Halogenated organic substrates are known to produce hydrogen halides (HF, HCl, HBr, and HI, collectively termed HX) as a by-product during the HTC process (Figs. 2 and 3).[7, 11, 23-26] Moreover, transfer of corrosive hydrogen halide gas through the analytical equipment may damage metallic components. Our experiments with the MS coupling confirmed the formation of HX from halogen-bearing compounds during EA-HTC.[7] As a consequence of incomplete $H_2$ yields, isotopic fractionation of up to several hundred milliureys was observed for seven compounds tested with EA-HTC-IRMS (Table 2). Similarly, hydrogen sulfide was observed as a by-product during EA-HTC of S-containing substances, with strong isotopic fractionation of $H_2$ measured with EA-HTC-IRMS (Table 2). Corrosive hydrogen sulfide is known to damage analytical equipment, either by sulfide formation on metal surfaces or after oxidation to sulfuric acid. The strong influence of hydrogen sulfide on the $H_3^+$-factor reduces the accuracy of hydrogen-isotope measurements.[11]

### *EA-Cr/HTC*

The formation of H-bearing conversion products other than $H_2$ was evaluated using the MS coupling with EA-Cr/HTC. In contrast to EA-HTC, no or only minor production of hydrogen halides was observed for EA-Cr/HTC. Similarly, no or only minor formation of H-bearing by-products other than $H_2$ was observed for EA-Cr/HTC of S-bearing substances. Overall, none of the analyzed substances yielded any by-products at abundances above the range of the air-water background, with the exception of silicon tetrafluoride ($SiF_4$) formed during the reaction of HF from F-bearing samples with $SiO_2$ in quartz wool. The observed $SiF_4$ did not significantly affect the hydrogen isotopic analysis. Using $Al_2O_3$ as the inner tube, we don't observe any fluorine-containing, gaseous by-product.

The $H_2$ yields of all analyzed substances were ≥ 96 % of the theoretical value (with a precision of ≤ 4 %).

## Hydrogen isotopic analysis *via* EA-Cr/HTC-IRMS

Hydrogen isotopic analysis was performed using either the solid or the liquid EA-Cr/HTC reactor setup. Samples were introduced into the EA depending on their physical characteristics either *via* direct liquid injection with a syringe or wrapped in silver capsules (Table 2). Water reference materials were injected with a syringe or were introduced in crimp-sealed segments of silver tubes.

### *Reference materials*

In contrast to our previous report, reference waters were successfully and consistently employed in EA-Cr/HTC for normalization of isotope data from solids and liquids according to the principle of identical treatment (IT) of sample and reference material.[7, 17] This improvement was possible because the modified reactor design with extended chromium filling avoided by-products and back-reactions of halogens and sulfur. The analytical precision of the $\delta^2$H values for waters was usually $1\sigma \leq 3$ mUr. Reference waters with a large range of $\delta^2$H values from –428 to +2555 mUr were utilized. The accuracy of the normalization to the VSMOW-SLAP scale was verified using GISP reference water and polyethylene foil IAEA-CH-7. The VSMOW-SLAP calibrated range was extended to +799.9 mUr [10] and +2555 mUr with $^2$H-enriched reference waters IAEA-604 and USGS W-89262 as a control anchor (Table 2). The isotopic composition of W-89262 was accurately reproduced with EA-Cr/HTC-, EA-HTC - and classical $H_2$-$H_2O$ equilibration – techniques, resulting in $\delta^2$H values of about +2555 ± 4 mUr. Remarkably, the low memory effect of the EA-Cr/HTC technique required less than five injections of VSMOW-water to revert back to correct $\delta^2H_{VSMOW} \equiv 0$ mUr values.

*Halogen-bearing compounds*

Multiple halogen-bearing compounds were analyzed using off-line and on-line techniques (Table 2). The uranium-based off-line conversion combined with DI-IRMS was applied for nine chlorine- and iodine-bearing substances, most of which were further used for validation of on-line EA-Cr/HTC-IRMS. Only theoff-line $\delta^2$H values from chlorine-rich *cis*-dichloroethene and trichloroethene were deemed unreliable due to incomplete $H_2$ yields. EA-Cr/HTC-IRMS achieved an overall precision of $1\sigma < 3$ mUr for $\delta^2$H values. The precision of $\delta^2$H values from solid samples was typically $1\sigma < 3$ mUr, such as for p,p'-DDD, p,p'-DDE, DDT, and γ-HCH. Several mono-halogenated benzenes (containing F, Cl, Br and I), 1,2-dibromoethene, and iodomethane were analyzed using EA-Cr/HTC-IRMS only (Table 2). No H-bearing by-products were detected after conversions, indicating quantitative conversion of organic hydrogen to $H_2$. The analytical precision of the $\delta^2$H values from these substances was in the range of $1\sigma \leq 1$ mUr.

Systematic ~50 mUr offsets between the off-line and on-line data were, however, observed for chloroethenes TCE and *cis*-DCE. The source of the difference is a non-quantitative conversion to hydrogen using the off-line method as described above for analytes with a high Cl/H molar ratios. Therefore, existing off-line and on-line methods should be generally evaluated with care for a quantitative conversion of the intramolecular hydrogen to $H_2$.

*Sulfur-bearing compounds*

Four S-bearing substances were analyzed, including the solids dimethyl sulfone and diphenyl disulfide, as well as the liquids dimethyl disulfide and thiophene (Table 2). The uranium-based off-line conversion was applied for the solids only and resulted in $\delta^2$H values with a precision of 1σ ≤ 4 mUr. The off-line values deviated by ≤ 4 mUr from the on-line values *via* EA-Cr/HTC-IRMS with a precision of 1σ ≤ 2 mUr. In addition, dimethyl disulfide and thiophene were analyzed *via* EA-Cr/HTC-IRMS with liquid injection in the LSI in Leipzig, resulting in a precision of 1σ ≤ 2 mUr.

## Stability of sequential on-line measurements

The analytical stability of the LSI-Leipzig EA-Cr/HTC-system was evaluated for reactor configurations for solid and liquid samples. About 200 Cl-bearing solid samples were run continuously using several carousels and resulted in $H_2$ yields of ≥ 96 % and a typical $\delta^2$H reproducibility of ±3 mUr (Tables S-1 and S-1a, Supplementary Information). Sequential analysis of more than 100 samples of liquid trichloroethene resulted in a precision better than ±4 mUr (Table S-2, Supplementary Information). Up to 270 sequential analyses *via* EA-Cr/HTC of various liquid halogen- and S-bearing compounds yielded a precision of better than ±3 mUr.

The reaction of hetero-elements with chromium is a surface reaction. Above 1250 °C, we observed $H_2$ peak broadening as a result of $H_2$ diffusing into and out of chromium granules.

## Hydrogen-isotope memory effects in EA-Cr/HTC

Small memory effects were generally observed during EA-Cr/HTC of halogen- and S-bearing compounds, similar to previous reports.[7, 11, 15] The memory was usually eliminated by rejecting the first and sometimes the second sequential data point. The memory effects increased with extended use of the chromium bed and seem to be useful as an indicator for the remaining reactor life time (Table S-3, Supplementary Information).

## CONCLUSIONS

Isotopic analysis of the same hydrogen-bearing substances using different apparatus resulted in different measurement results outside the analytical uncertainties, indicating methodological uncertainties. Routine EA-HTC (TC/EA) instrumentation did not provide quantitative hydrogen conversion of several heteroelement-bearing (N, S, X) compounds. In addition, a classical off-line method failed to provide quantitative hydrogen conversion for highly chlorinated ethenes (DCE and TCE).Different results from various methods for the same substances indicated methodological uncertainties. The routine EA-HTC (TC/EA) method does not provide quantitative conversion of several heteroelement-bearing (N, S, X) compounds. In addition, classical off-line conversion was observed to fail for highly chlorinated ethenes (DCE and TCE).

The improved on-line EA-Cr/HTC reactor design incorporates a chromium-filled section spanning an extended temperature zone from ≥ 1200 °C at the top to < 200 °C at the bottom. Cooler chromium near the outflow more effectively immobilizes halogens as $Cr_xX_y$ (where X is F, Cl, Br, or I) and sulfur as $Cr_xS_y$. As a result, the pyrolytic $H_2$ yield from water and organic compounds is optimized and isotopic fractionation is minimized. No significant amounts of H-bearing by-products of organic pyrolysis were detected. Analyses of water reference materials can be interspersed with organic analytes for improved isotopic normalization of $\delta^2$H values according to the principle of identical treatment of sample and reference material. The use of a graphite crucible improves the separation of metal and carbon debris from chromium, which reduces the danger of chemical deactivation of chromium and the blockage of gas flow. The improved EA-Cr/HTC reactor design offers a reliable and economic approach for measuring the $\delta^2$H values of chemically complex organic analytes, regardless of gaseous, liquid, or solid state. The universally applicable methodology should prove especially advantageous for analysis of anthropogenic halogen- and sulfur-bearing compounds having environmental significance.

### Author contributions

This manuscript includes contributions from all authors. All authors have given their approval of the present version of this manuscript.

Notes:

The authors declare no competing financial interests.

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## Supporting information

Additional supporting information may be found at Gehre et al. [28]

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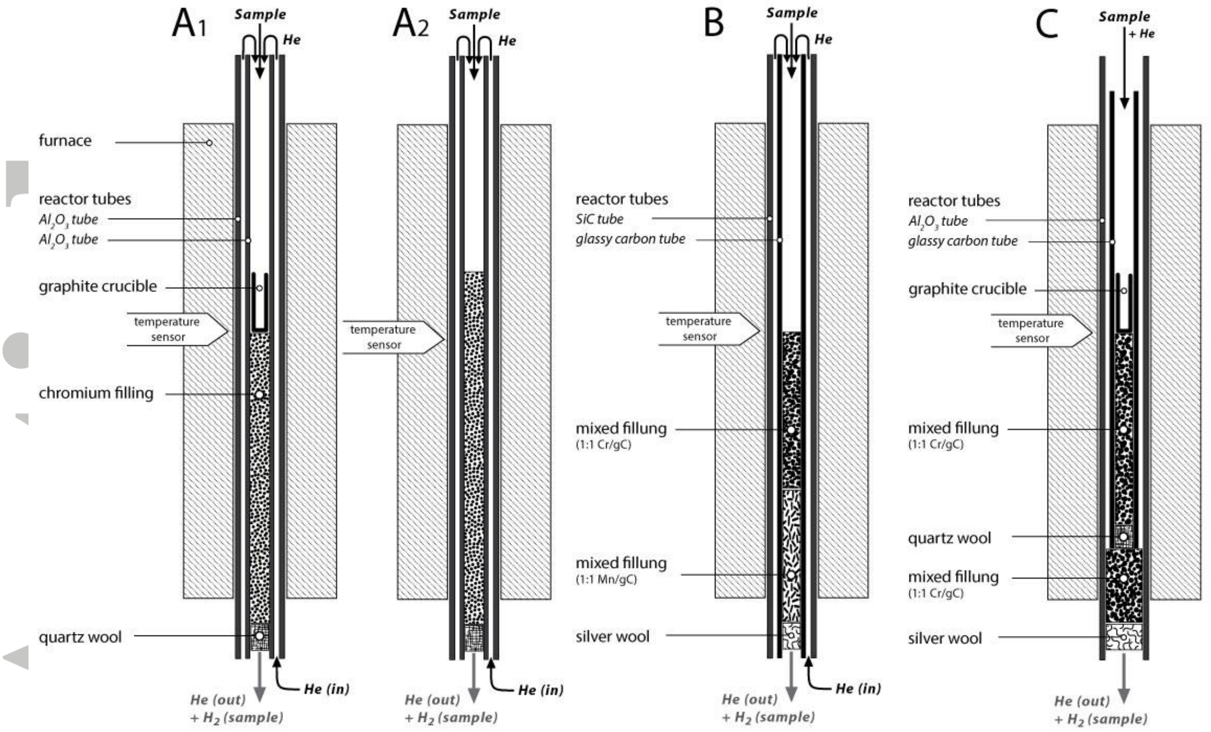

**Figure 1:** Applied EA-Cr/HTC reactor designs in different laboratories. (A) Modified tube-in-tube reverse-flow reactor at LSI Leipzig, for (A1) solid injection and (A2) liquid injection, (B) tube-in-tube reverse-flow reactor at BGC-ISOLAB Jena, (C) tube-in-tube reactor at RSIL-USGS Reston.

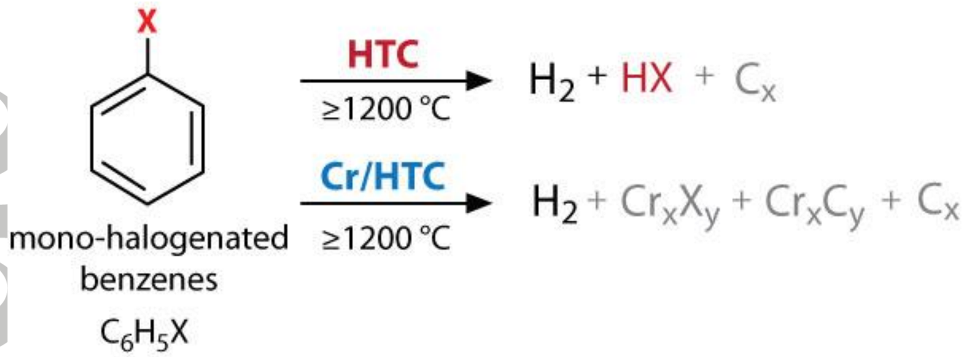

**Figure 2:** Principles of conversion from mono-halogenated benzenes to molecular hydrogen and by-products (stoichiometry unknown).

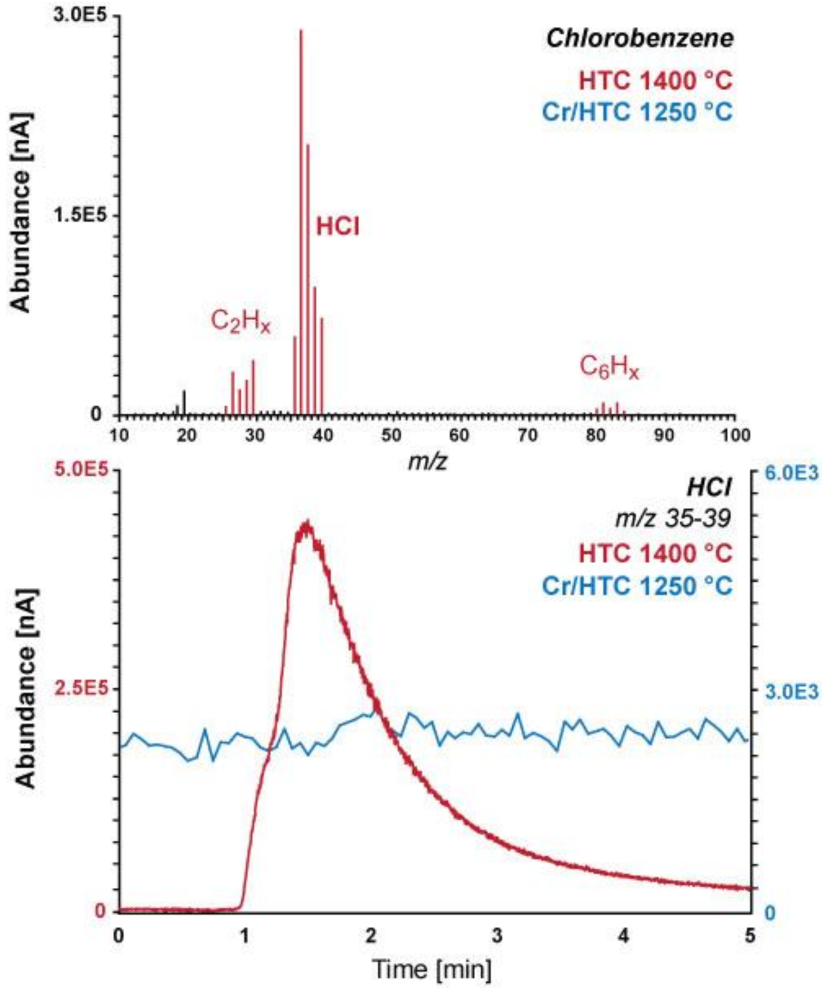

**Figure 3:** By-product formation during EA-HTC (red) and EA-Cr/HTC (blue) of chlorobenzene as detected by mass-spectrometric ion-trap monitoring of the reactor effluent.

**Table 1:** Itemized problems, consequences, and remedial solutions for EA-Cr/HTC reactor design for solid and liquid samples.
[*only for solid samples.]

| | **Problem** | **Consequence** | **Solution** |
|---|---|---|---|
| 1.* | Coating of chromium by silver | Inactivation of chromium, incomplete conversion to $H_2$ if silver coats chromium | Graphite crucible or 10 mm of quartz wool above the chromium traps silver |
| 2.* | Reactor blockage by carbon and ash from pyrolysis | Blockage of the carrier gas flow and enlarged carbon surface in reactor | Trapping of ash in graphite crucible, Cr-particles with 1–3-mm diameter reduce blockage |
| 3. | Chromium reacts to form halides and sulfide | Mobile chromium salts block carrier gas flow | Chromium particles with 1–3-mm diameter ensure constant carrier gas flow over >250 samples |
| 4. | Incomplete conversion within chromium | Formation of H-bearing byproducts and inaccurate H-isotopic analysis | Extension of the chromium filling down to the bottom of the reactor |
| 5. | Restricted measurements of reference waters | Back-reaction of halogens (X) from Cr-halides to HX after processing of halogen-bearing samples | Extension of the chromium filling down to the bottom of the reactor |
| 6. | Quartz reactors soften and become dysfunctional at >1250 °C | Quartz reactors limit the conversion temperature. | $Al_2O_3$ ceramic reactors can operate at up to 1900 °C |
| 7. | Quartz reactors are not reusable | Short life span of quartz reactors entails maintenance and expense | $Al_2O_3$ ceramic reactors can be re-used, due to high thermal stability |
| 8. | Reaction of quartz with fluorinated compounds | Formation of $SiF_4$ gas damages quartz reactor | Use of $Al_2O_3$ ceramic avoids formation of $SiF_4$. A reaction of F with Al to $AlF_3$ is thermic stable at ~1300 °C |
| 9. | Chromium salts are hygroscopic | Reactor can be damaged when hygroscopic chromium salts expand in contact with moisture | Remove Cr-filling as soon as possible after cooling |

**Table 2:** Hydrogen isotopic analysis of several halogen- and sulfur-bearing compound classes. The $\delta^2$H values from three analytical methods: off-line (DI-IRMS) in one laboratory and on-line (EA-Cr/HTC *vs* EA-HTC) determined in three different stable isotope laboratories. All results are normalized to the VSMOW-SLAP scale.

| | | | | **off-line DI-IRMS** *Indiana University* | **on-line EA-Cr/HTC-IRMS** *LSI Leipzig* | | **on-line EA-Cr/HTC-IRMS** *BGC-ISOLAB Jena* | **on-line EA-Cr/HTC-IRMS** *RSIL USGS* | **on-line EA-HTC-IRMS** *LSI Leipzig* |
|---|---|---|---|---|---|---|---|---|---|
| **Compound** | **Formula** | **Supplier** | **Purity [%]** | **$\delta^2$H [mUr]** | **$\delta^2$H [mUr]** | ***$H_2$ yield* [%]** | **$\delta^2$H [mUr]** | **$\delta^2$H [mUr]** | **$\delta^2$H [mUr]** |
| VSMOW2 | $H_2O$ | IAEA | | 0 ± 1.1 | 0 ± 2 | 100.0 ± 4.0 | - | - | 0 |
| SLAP2 | $H_2O$ | IAEA | | -427.5 ± 3 | -427.5 ± 2 | - | - | - | -427.5 |
| GISP | $H_2O$ | IAEA | | - | -190.4 ± 1.4 (23) | - | - | - | -189.5 |
| IAEA-604 | H2O | IAEA | | +799.9 | +800 ± 2 | - | - | +799.9 ± 8.4 (7) | - |
| W-89262 | H2O | USGS | | - | +2551.5 ± 4.0 (15) | - | +2561.5 ± 8.0 (16) | - | +2555 |
| UC04 | H2O | USGS | | - | - | - | - | +113.6 ± 3.2 (10) | - |
| Polyethylene foil IAEA-CH-7 | $[-CH_2-]_n$ | IAEA | | -97.6 ± 1.3 | -101.3 ± 0.9 (12) | 100 ± 2.0 | -98.0 ± 0.6 (30) | - | -100 |
| ***Fluorine-bearing*** | | | | | | | | | |
| Fluorobenzene | $C_6H_5F$ | Aldrich | 99 | - | -334.0 ± 2.6 (19)* | 98.3 ± 0.9 (8) | - | - | - |
| ***Chlorine-bearing*** | | | | | | | | | |
| Chlorobenzene | $C_6H_5Cl$ | Bernd Kraft | 99 | - | +39.8 ± 2.9 (19)* | 99.1 ± 1.0 (4) | +36.4 ± 4.0 (13)* | - | - |
| p,p'-Dichlorodiphenyldichloroethane | $C_{14}H_{10}Cl_4$ | ABCR | 98 | +72.0 ± 1.2 (5) | +72.8 ± 2.3 (11) | 97.4 (4) | +75.1 ± 2.5 (5) | - | -30 |
| p,p'-Dichlorodiphenyldichloroethylene | $C_{14}H_8Cl_4$ | ABCR | 99 | -81.6 ± 2.0 (6) | -83.9 ± 3.2 (13) | n.d. | -83.7 ± 0.2 (5) | - | -99 |
| 4,4'-Dichlorodiphenyltrichloroethane | $C_{14}H_9Cl_5$ | Supelco | 97 | -13.9 ± 0.8 (4) | -16.4 ± 2.9 (12) | 96.6 (4) | -14.7 ± 2.0 (4) | - | +252 |
| γ-Hexachlorocyclohexane | $C_6H_6Cl_6$ | HiMedia | 99 | -74.0 ± 3.2 (4) | -77.4 ± 2.2 (13) | >98.0 (50) | -81.4 ± 4.0 (5) | - | +356 |
| 1,1,2-Trichloroethene | $C_2HCl_3$ | PPG | 99 | +466.1 ± 20.8 (4) | +513.9 ± 3.1 (30)* | - | +508.6 ± 2.5 (19)* | - | +122 |
| 1,1,2-Trichloroethene | $C_2HCl_3$ | Merck | 99 | +593.4 ± 7.3 (4) | +641.0 ± 2.1 (23)* | - | +641.9 ± 3.4 (16)* | - | +173 |
| 1,1,2-Trichloroethene | $C_2HCl_3$ | Sigma-Aldrich (AS) | 99.5 | +505.6 ± 2.1 (5) | +548.2 ± 7.0 (16)* | 97.5 ± 2.2 (6) | - | +533.6 ± 1.4 (6) | - |
| *cis*-Dichloroethene (#2) | $C_2H_2Cl_2$ | CHEMOS (AS) | 99 | +728.7 ± 2.4 (4) | +774.1 ± 2.4 (19)* | 98.8 ± 2.8 (6) | - | +795.3 ± 4.4 (5) | - |

|  |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
| ***Bromine-bearing*** |  |  |  |  |  |  |  |  |  |
| Bromobenzene | $C_6H_5Br$ | Merck | 99 | - | -8.3 ± 2.6 (18)* | 96.6 ± 1.4 (8) | -11.3 ± 2.0 (13)* | - | - |
| 1,2-Dibromoethene | $C_2H_4Br_2$ | Sigma-Aldrich | 99 | - | -59.6 ± 1.2 (25)* | 97.5 ± 3.5 (8) | -63.9 ± 1.1 (12)* | - | - |
| ***Iodine-bearing*** |  |  |  |  |  |  |  |  |  |
| Iodobenzene | $C_6H_5I$ | Merck | 99 | - | -79.0 ± 2.4 (19)* | 98.8 ± 0.7 (8) | -82.1 ± 1.6 (12)* | - | - |
| Iodomethane (#1) | $CH_3I$ | Sigma-Aldrich (AS) | 99.5 | -95.6 ± 1.2 (6) | -99.2 ± 2.3 (16)* | 100.8 ± 2.5 (8) | - | - | - |
| ***Sulfur-bearing*** |  |  |  |  |  |  |  |  |  |
| Dimethyl sulfone | $C_2H_6O_2S$ | Alfa Aesar | 99 | +133.9 ± 2.7 (4) | +130.0 ± 1.4 (11) | - | +133.3 ± 1.4 (5) | - | +292 |
| Diphenyl disulfide | $C_{12}H_{10}S_2$ | Sigma-Aldrich | 99 | -148.4 ± 4.0 (5) | -156.7 ± 3.4 (11) | - | -157.5 ± 2.2 (5) | - | +771 |
| Dimethyl disulfide | $C_2H_6S_2$ | Aldrich | 99 | - | -178.4 ± 2.4 (15)* | 98.4 ± 2.5 (8) | -178.9 ± 2.5 (20)* | - | - |
| Thiophene | $C_4H_4S$ | ABCR | 99 | - | +62.1 ± 1.9 (15)* | 100.8 ± 1.4 (8) | +56.9 ± 3.0 (13)* | - | - |

-: not determined; *: liquid injection; AS: Arndt Schimmelmann