Gilevska, T., Sullivan Ojeda, A., **Renpenning, J.**, **Kümmel, S.**, **Gehre, M.**, **Nijenhuis, I.**
(2020):
Requirements for chromium reactors for use in the determination of H isotopes in compound-specific stable isotope analysis cf chlorinated compounds
Anal. Chem. **92** (3), 2383 – 2387

http://dx.doi.org/10.1021/acs.analchem.9b04737

Requirements for chromium reactors for use in determination of H isotopes in CSIA of chlorinated compounds

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KEYWORDS: hydrogen CSIA, Cr reactor, halogenated contaminants

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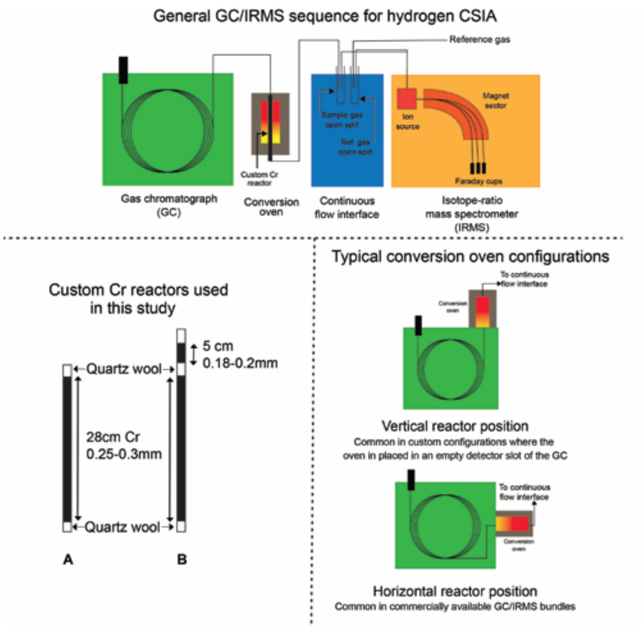
ABSTRACT: There is a strong need for careful quality control in hydrogen compound-specific stable isotope analysis (CSIA) of halogenated compounds. This arises in part due to the lack of universal design of the chromium (Cr) reactors. In this study, factors that optimize the critical performance parameter - linearity - for the Cr reduction method for hydrogen isotope analysis were identified and evaluated. These include the effects of short and long vertically-mounted reactors, and temperature profiles on trapping of Cl to ensure accurate and precise hydrogen isotope measurements. This paper demonstrates the critical parameters that need consideration to optimize any Cr reactor applications to assure the accuracy of δ^2H analysis for organic compounds and to enhance intercomparability for both international standards, and for reference materials run by continuous flow versus elemental analyser.

Compound-specific stable isotope analysis (CSIA) has become an increasingly important tool in characterizing sources, fate, and transformation mechanisms of organic contaminants.[1] Analytical techniques for CSIA evolved to include evaluation of carbon, chlorine, and nitrogen isotope ratios of organic compounds that are often targets of remediation efforts[2] These, combined with hydrogen CSIA of chlorinated contaminants[3–10] can provide useful information to discriminate between reaction mechanisms.[11] Large primary isotope effects, due to large differences in bond strength of ^1H vs ^2H, can be expected where hydrogen is directly involved in the rate-limiting step (e.g. carbon-hydrogen bond oxidation).[1] However, secondary isotope effects can also support reactive mechanism identification (e.g. secondary hydrogen isotope effects have confirmed anaerobic biodegradation of MTBE via an S_N2 reaction mechanism[12]). Furthermore, including hydrogen CSIA as one of multiple elements analyzed for a given contaminant can provide two or three-dimensional isotope plots useful for characterizing degradation processes and source characterization.[2–4,8,11,13]

Hydrogen isotope ratios of non-halogenated compounds using CSIA are typically analyzed using a gas chromatograph (GC) coupled to a high temperature conversion (HTC) oven at 1400-1500 ºC, followed by the measurement of the produced hydrogen gas by an isotope-ratio mass spectrometry (IRMS).[14] However, for halogenated compounds, this method can induce isotope fractionation artifacts due to incomplete conversion of the compound to H_2 and simultaneous formation of byproducts, e.g. HCl.[15] The formation of HCl is undesirable because of its corrosive nature and resulting need for frequent instrument maintenance.[15] The Cr-based reactor method was developed to circumvent these problems for elemental analyzer (EA-IRMS) applications[16–18] and has been since applied to CSIA.[9,10,19,20] The lack of commercially available Cr reactors and differing instrument configurations for GC-Cr/HTC-IRMS instruments require that each laboratory create a customized setup for hydrogen CSIA. The general setup involves 3 parts, 1) GC, 2) continuous flow control system, and 3) IRMS (Figure 1). Custom instrument configurations often have the HTC oven in a detector slot of the GC, creating a vertical oven position. Commercially available GC/IRMS bundled systems often have a horizontal HTC oven pre-arranged on the side of the GC box. For customized Cr reactors, variations in the design include particle size (≤0.2mm[10], ≤0.25mm[9] or between 0.25-0.3mm[19,20]), temperature of the conversion oven (1400°C,[19] 1200°C,[20] 1000°C,[10] or 850°C[9]), and length of the Cr packing (13 cm,[9] 24 cm,[19] 28 cm[20], or 30 cm[10]). Nevertheless, the principle for all instrument configurations and reactors is similar: Cr powder quantitatively converts halogenated compounds into H_2, while scavenging nitrogen, oxygen, sulfur and halogens. [9,16,19,20]

Figure 1. Schematic shows general GC-IRMS instrumental setup (top) and a vertical and a horizontal conversion oven configuration (bottom right). Custom Cr reactors used in this

study are shown in bottom left: A) short reactor design (identical to ref. 20), and (B) long reactor design with additional 5 cm Cr for trapping Cl. All modifications are based on common IRMS components.



This technical note describes the critical parameters essential to achieve optimized and consistent linearity – a critical component in ensuring precision and accuracy for hydrogen CSIA.[3–8,13,21] The basic reactor design from Renpenning et al.[19,20] was chosen as it has been demonstrated to achieve quantitative conversion of organic-bound hydrogen to H_2 and produced symmetric and narrow peaks suitable for chromatographic separation. The latter is beneficial for field samples with complex matrices, where many non-target compounds need separation from the target analyte(s). Here however, the previously reported settings[20] were modified to accommodate differences in the reactor oven position and to examine vertically aligned rectors (Fig. 1), comparing both short and long reactor lengths. As there is no universal design of chromium reactors for hydrogen isotope analysis, our results provide practical guidance for those using Cr conversion to ensure linear (and therefore accurate and precise) hydrogen isotope analysis and the essential intercomparability of results between isotope laboratories worldwide. Chlorobenzenes were chosen as model compounds to study the reactor performance as they are frequently encountered as soil and groundwater contaminant[22,23] and had no offset between bulk (EA) and CSIA Cr conversion.[20]

Experimental section

Instrumentation

Stable hydrogen isotope analysis with vertical oven position was performed by GC-Cr/HTC-IRMS (Hewlett-Packard 6890 GC connected via a combustion interface to a Finnigan MAT Delta plus XL IRMS). A VOCOL (Supelco, 60 m × 0.32 mm, 1.8 µm film thickness) GC column using temperature program described earlier.[23] The injector temperature was 180 °C with a fixed column flow of 1.5 ml/min. Samples were injected by direct liquid injection into a split/splitless injector to test the conversion process and to exclude any fractionation effects that can occur during preconcentration methods like purge and trap or solid phase microextraction. The conversion oven was at 1200 ºC. The H_3^+ factor is the correction factor, accounting for the contribution of H_3^+ ions to the HD^+ beam over the range of the ion source pressures in the mass spectrometer. The H_3^+ factor was monitored twice daily to observe the influence of HCl, which may sorb on metal surfaces, especially in the presence of water.[24] A small but most importantly stable H_3^+ correction is essential to ensure linearity and accuracy of δ^2H analysis. The presence of HCl was measured by manually entering m/z 36 on the center cup of the IRMS, immediately after the compound was eluted from the GC and detected at the IRMS.

EA-Cr/HTC-IRMS (a EuroVector EA 3000 connected to a Thermo Fisher MAT 253 IRMS) measurements were performed as described previously using a conversion temperature of 1250 ºC.[17] Analysis of pure compounds (monochlorobenzene (MCB), 1,2-dichlorobenzene (1,2-DCB), 1,3-dichlorobenzene (1,3-DCB), 1,2,4-trichlorobenzene (1,2,4-TCB) were performed over several days in triplicate. Raw data were normalized via standard two-point calibration on VSMOW-SLAP scale.[25]

Cr reactor design

Two Cr reactor designs were tested in the study. The short vertical reactor (Figure 1, A) was identical to the one previously investigated while installed in a horizontal position.[19,20] Briefly, a tubular ceramic reactor (32 cm, 0.8 mm i.d., 1.6mm o.d.; Degussit AL23 aluminum oxide ceramic; Friatec) was filled with Cr powder (purity 99%, particle size 0.25-0.30 mm, Cr Patinal, Merck). Both ends of the reactor were plugged with quartz wool (Elemental Microanalysis). For the long vertical reactor design (Figure 1, B) a 37 cm tubular ceramic tube of the identical material was used. The same length of the reactor was filled with Cr powder (particle size 0.25-0.30 mm), followed by 1 cm quartz wool stopper. In this case however, the last 5 cm of the reactor were filled with smaller Cr particles (particle size 0.18-0.20 mm, Patinal, Merck). The end of the reactor was plugged with quartz wool. The long reactor design extended beyond the length of the high-temperature oven by about 7 cm. To achieve particular ranges of chromium grain size, the chromium was put through set of a sieves. A small amount of 0.25-0.30 mm is collected after sieving. For both reactors the carrier gas flow becomes restricted at higher temperatures. Despite the difference in the amount of Cr, both designs restricted column flow by approximately 20% (from 1.5.ml/min to 1.2 ml/min).The temperature profile of the reactor was measured with a K type thermocouple (Eutech Instruments).

2-point-calibration

The measured δ^2H values from GC-Cr/HTC-IRMS were normalized to the values from EA-Cr/HTC-IRMS using the 2-point calibration method[26] with 1,2-DCB and 1,3-DCB as the calibration anchors (Table 1). Accurate determinations of δ^2H

via two-point normalization use at least two isotopic reference materials to (i) anchor the isotopic scale and (ii) compensate for differences in responses of instruments, which commonly compress isotope−δ scales. [26]

Results and Discussion

GC-Cr/HTC-IRMS

Accurate hydrogen isotope measurements of organic compounds require quantitative conversion to H_2. A previous study investigated this using the horizontal reactor set-up (Figure 1, bottom) with 28cm of Cr powder particle size of 0.25-0.30 mm in the reactor and temperature 1200ºC and found no evidence of byproducts (primarily HCl), indicating quantitative conversion.[20] Even in the case of efficient conversion however, trapping of the HCl products is essential as excessive HCl released into the IRMS results in hydrogen isotope data consistently offset from the "true" values, contributing to a non-linear response.[19] This study investigates how aspects of reactor design can improve linearity and demonstrates the effect of the critical parameters H_3^+, accuracy and precision, with implications for calibration, and intercomparison with reference measurements characterized by EA/IRMS.

HCl formation versus H_3^+ stability

Some byproducts are known to influence the H_3^+factor, resulting in less accurate hydrogen isotope measurements via IRMS.[27] We observed that a symptom of the incomplete trapping of HCl by the reactor was the increase in the m/z 36 (due to HCl), and a resulting shift in the H_3^+ factor. The principle of HCl formation in Cr reactors is discussed in previous publications.[17,20] Briefly, Cr halides are thermally less stable than Cr carbides, nitrides, or oxides, therefore continuous combustion of organic compounds into the Cr reactor may gradually displace the thermally less stable Cr-halides, pushing Cr-halides toward the end of the reactor and eventually cause the release of the formed HCl (SI, Section 2).

H_3^+ factors for the short reactor increased by 0.5 (from 5.5 to 6) after 53 injections (Figure 2). After 83 and 107 injections the H_3^+ factor for the short reactor increased by 2.5 and 4, respectively. This change in H_3^+ corresponded to m/z 36 of 1050 mV, measured after injection. In contrast, the long reactor produced a constant H_3^+ factor, with a change of 0.5 only, after 153 injections. Even after 276 injections the change in m/z 36 and H_3^+ factor were only100 mV and 1, respectively (Figure 2). This demonstrates much longer lifetime and larger capacity of the long reactor to trap produced HCl. Furthermore, the signal areas increased roughly 3 to 6-fold for the same amount of H_2 injected on column for the long reactor compared to the short, which also indicates better management of HCl (Figure S1, Table S1).

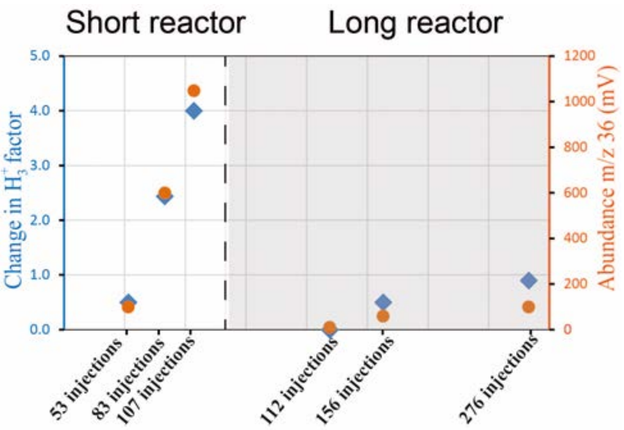


Figure 2. Correlation between changes in H_3^+ factor (blue diamond), abundance of the m/z 36 (HCl) (orange circles) and number of injections per short and long reactor.

Cr reactors in the vertical (this study) or horizontal position[20] reach the same maximum temperature zone (1200 ºC), above the necessary threshold for complete conversion of organic-bound hydrogen to H_2.[20] In addition to a "hot zone" for conversion, reactors require "cold zone" for trapping. The main difference between the reactor positions was the temperature gradient of reactive Cr. In the horizontal position the end of the reactor reaches a temperature of ~ 200 ºC, which provides an important temperature zone cold enough for halogen trapping (Figure 3).[20] In contrast, in the vertical position a "chimney effect" was induced by the carrier gas. Thus, the end of the Cr packing was hotter (~ 350 °C) than optimal for the immobilization of chlorine, and the excess of produced HCl entered the mass spectrometer. In the vertical position (Figure 1, B) this "cold zone" (temperatures down to 60ºC) was improved by adding 5cm of Cr packing, allowing the reactive halides to be trapped as effectively as in the horizontal setup.

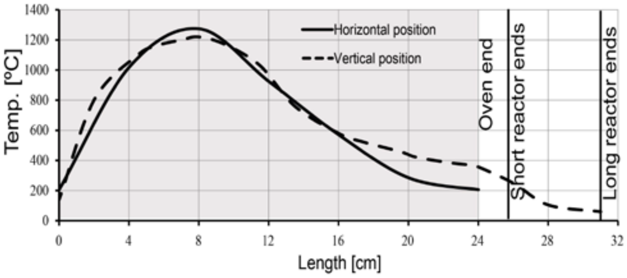


Figure 3.Temperature profile for horizontal reactor position (solid line) from Renpenning et al. [20] and vertical reactor position (dashed line). Shaded area represents temperature profile measured inside the oven set up for 1200°C.

Precision and accuracy

The comparison between the different reactor designs for all measured compounds is presented in Table 1 and Figure S2. In case of the shorter reactor, the mean measured values of 1,3-DCB is within 5‰ of the mean values measured via EA-Cr/HTC-IRMS, whereas the values for MCB (only for vertical),1,2-DCB and 1,2,3-TCB showed a shift of -7 to -9‰ compared to the EA-Cr/HTC-IRMS values. To achieve precise and accurate values, the long reactor was required resulting in MCB, 1,3-DCB and 1,2-DCB and 1,2,4-TCB that were all within 5‰ of the values measured via EA-Cr/HTC-IRMS.

For the short reactor, 2-point calibration could correct the offset with EA-Cr/HTC-IRMS results, making the values consistent and reproducible within standard deviations of ±5‰. It is tempting in this case to use 2-point calibration to correct for offsets. However, if the reason for the bias is not known and the result is overproduction of HCl, then potential damage can be caused to the ion source of the mass spectrometer. It is more advantageous to address this issue directly by the design optimizations described here than to solely rely on a 2-point calibration correction.

Past studies investigated trapping of HCl after conversion by using liquid nitrogen at the end of the reactor.[9,15] Trapping of produced HCl after the conversion by liquid nitrogen protected the source from corrosive compounds, but did not eliminate isotope fractionation artifacts due to incomplete conversion. In contrast, trapping halides in a “cold zone” on the Cr reactor removes the need to quantify and correct for analytical bias that occurs during the conversion process and is a more reliable method than liquid nitrogen trapping.[9,15]

Table 1. Hydrogen isotope values of chlorinated benzenes measured by GC- Cr/HTC-IRMS with either the 32 cm(short) or 37 cm (long) Cr reactor and by EA-Cr/HTC-IRMS; n- number of measurements; M- measured values; Cal.- calibrated values.

	GC-Cr/HTC-IRMS						EA
	δ^2H [‰] vertical		δ^2H [‰] horizontal		δ^2H [‰] vertical		δ^2H [‰]
	Short reactor				Long reactor		
	M	Cal.	M	Cal.	M	Cal.	Cal.
MCB	40±5 n=21	48±6 n=21	46±1 n=7	48±3 n=7	47±5 n=21	47±6 n=21	49±2 n=23
1,2-DCB	59±5 n=25	67±4 n=25	60±6 n=7	65±5 n=7	68±2 n=15	68±3 n=15	67±1 n=24
1,3-DCB	-122 ± 5 n=25	-121 ± 4 n=25	-122 ± 4 n=7	-124 ±5 n=7	-124 ± 2 n=16	-120 ± 1 n=16	-120 ± 2 n=24
1,2,4-TCB	103± 6 n=24	114±5 n=24	102± 1 n=6	109± 1 n=6	116±4 n=5	116±4 n=5	111± 1 n=16

Conclusions and Recommendations

The position of the reactor, Cr particle size, and temperature profiles of the reactors vary between reported GC-Cr/HTC-IRMS applications and published studies. However, the fundamental principles for accurate and precise δ^2H analysis via Cr reduction are the same and are highly dependent optimized linearity that is consistent over time. First, there is a temperature threshold (“hot zone") that must be reached for conversion of the compound to H_2.[20,24] While, the temperature is an important parameter for conversion, Cr particle size and length of packing, column flow also have to be taken into account in conversion optimization.[19] Second, a "cold zone" must exist to trap of all the heteroatoms after the conversion. Efficient managing of HCl formation can be achieved by optimizing a combination of parameters (Cr particle size, temperature profile, reactor position), which influence the efficiency of trapping and thermal stability of the reactive byproducts. In this study, increasing the length of the reactor from 32 to 37 cm with an additional Cr zone (5 cm of 0.18-0.2mm Cr), has produced a cold zone for trapping Cl. Increasing the length of Cr filling did not result in higher flow constriction or changes to the peak shape and did not adversely influence the chromatography (Figure S3, S4). Therefore, we have not observed any disadvantage caused by the increasing length of the reactor and in fact increase in sensitivity can be achieved. Although these trends were observed for chlorobenzenes, we expect other halogenated compounds to show the same types of linearity issues such as large deviations in the H3+ factor. For different particle sizes of Cr (and hence reactive surfaces), a different temperature profile will likely be required to trap halides in the Cr reactor. It is advised to monitor the production of HCl daily by GC-MS or GC-IRMS to ensure this reactive product is not produced in elevated amounts. Compound specific standards with the range of isotopic signatures and chemical composition are advantageous to use when testing the performance of a reactor as different compounds may behave differently during conversion by Cr. While proper calibration, using two-point normalization is recommended[26], the design modifications outlined here ensure better linearity (and longevity and long-term performance) for both routine measurements and for successful calibration.

GC-Cr/HTC-IRMS has been proven to be the most reliable technique for hydrogen CSIA of halogenated compounds.[9,10,19,20] As there is no uniform method for the Cr reactor design or instrumentation, accuracy and reproducibility of results and community intercomparison requires this investigation of the major parameters determining performance. This study has demonstrated how reactor design impacts the critical performance issue of Linearity (through the related parameters H_3^+, accuracy and precision, and hence calibration vis a vis international standards, and deviation from reference measurements by EA/IRMS). The study also demonstrated the effect of temperature profiles, trapping efficiency (via amount of HCL detected), and reactor longevity. This information is vital for ensuring performance by individual laboratories and within the global community increasingly applying multi-isotope (2D

(C and H, or C and Cl), or even 3D) isotope analysis to the interpretation and monitoring remediation of contaminants, including not only chlorinated benzenes but the wide variety of other chlorinated solvent contaminants to which IRMS analysis is currently applied.

SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website

Comparison of peak areas and δ^2H values between reactors, chromatogram traces.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Many thanks to Elizabeth Phillips and Oliver Warr for the discussion on the paper. The research was supported by the DAAD (German Academic Exchange Service) from funds of the German Federal Ministry of Education and Research (BMBF) (PPP Kanada 2017 Project-ID 57315688; HALOGEN) and by Natural Sciences and Engineering Research Council (NSERC) Discovery Grant funded to Barbara Sherwood Lollar

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