TECHNICAL NOTE 30806

EA-IRMS: Hydrogen isotope analysis of S/N/halogens bearing samples by chrome reactor

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Keywords: Elemental analysis, chrome reactor, hydrogen

Goal

Demonstrate the benefits of using chrome reactor for hydrogen analysis of S/N/halogens bearing samples.

Introduction

Chrome (Cr) has been identified as a perfect reduction material in reactors many years ago.[1,2] It replaced the somewhat impracticable reduction of H_2O on metals such as Zinc or Uranium. Both materials were widely used for water analysis until the introduction of glassy carbon for elemental analysis. The glassy carbon reactor allowed automated, high-throughput isotope analysis of solids and liquids in continuous flow resulting in both, Oxygen (O) and Hydrogen (H) isotope ratios. This advantage of glassy carbon over Cr has resulted in simultaneous OH isotope analysis being reported in more than 1,000 publications over the past 20 years. Several publications[3,4] since have reported discrepancies in isotope values when analyzing substances with both techniques, Cr reduction and glassy carbon reduction. Recent findings[5,6] showed that complete conversion of H-containing substances to H_2 gas are inhibited if hetero-atoms, such as Sulfur (S) or Nitrogen (N) or halogens, are present forming H-N, H-S or H-Cl compounds. This promoted using Cr reactor filling for performing analysis of H isotope ratios on S/N/halogens containing samples.

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Instrument setup

The Thermo Scientific™ EA IsoLink™ IRMS System enables the analyses of hydrogen isotopes using a Cr reactor in the EA IsoLink OH IRMS configuration or the extended CN(S)OH configuration. The standard ceramic tube in the high-temperature furnace remains untouched but the glassy carbon tube should be replaced by a quartz glass tube of the same dimension (355 mm L, 12 mm OD and 7 mm ID). The quartz glass tube is an inexpensive solution for Cr granules as the tube needs to be discarded after analysis because Cr granules inside bake together, preventing re-use of the tube. The filling heights remain the same as with the glassy carbon granules. Cr granules used for the analysis presented here were of 3-5 mm in size. They are mixed with conventional glassy carbon chips with a ratio of 1:1. The furnace temperature was set to 1,200 ˚C during analysis.

Thermo Scientific™ AS 1310 Liquid Autosampler offers a versatile solution for automated injection of 100 nL of water with a 0.5 µL syringe. One wash and five strokes from a 1.2 mL vial are sufficient to remove any remains of the previous sample in the syringe as indicated by the negligible memory effect in Figure 1. Up to 800 sample injections are possible with one reactor filling.

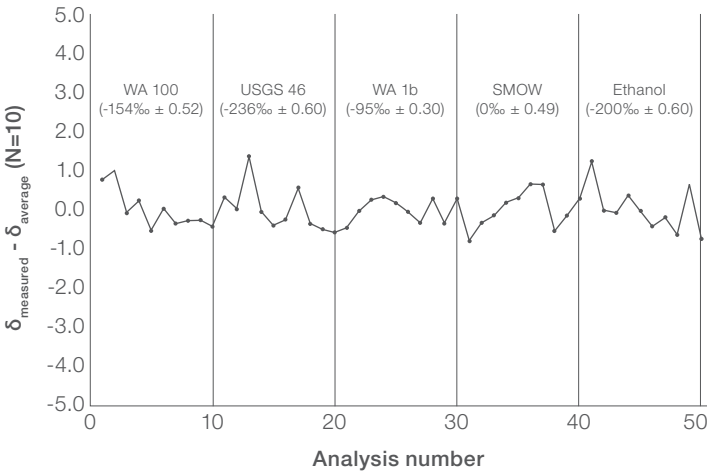

Figure 1. Memory effects of a sequence of water analyses with 10 repetitions displayed as a difference between measured and the mean value of N=10 (data in brackets).

Results

Efficiency of hydrogen analysis is shown in Figure 2, demonstrating analysis of 100 nL of USGS46 water standard within 110 s.

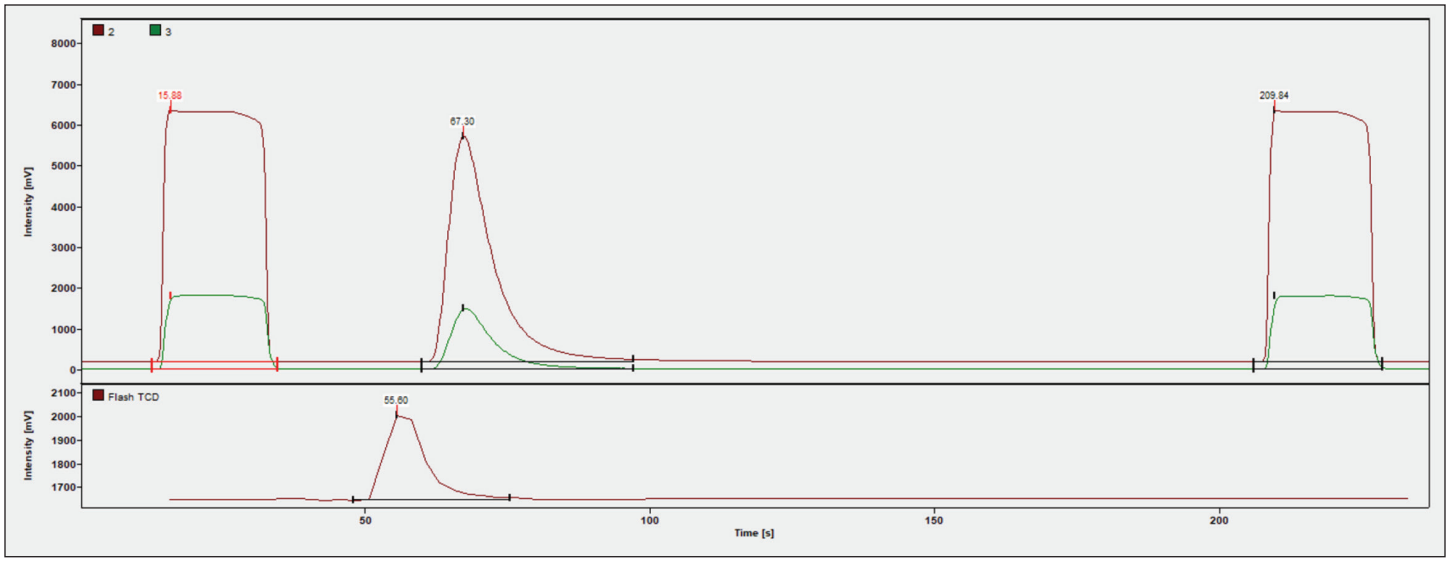

Figure 2. Example chromatogram of 100 nL injection of USGS46 water standard. Mass traces of *m/z* 2 and 3 (above) as well as TCD trace (below) are shown. Squared pulses at the beginning and end of the chromatogram are reference gas injections. The second reference gas is not mandatory reducing the net analysis time to 110 s.

Precision of the hydrogen analysis by using Cr reactor filling and memory effects are investigated by analysis of five different samples measured in 10 repetitions. The data presented in Figure 1 indicate high precision and negligible memory effect.

Stability of the hydrogen isotope analysis using Cr reactor was investigated over a 4-day period by performing continuously 10 consecutive water injections (100 nL/injection) of four different samples resulting in a total of 950 injections. Mean delta values of 10 consecutive injections of the same four samples at the beginning and at the end of the run are displayed in Figure 3. The results show no discrepancy in hydrogen isotope values acquired at the beginning versus the values acquired at the end of the sequence.

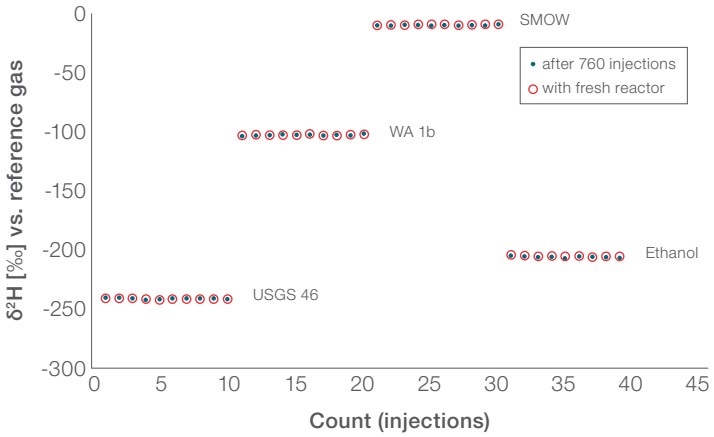

Figure 3. Stability of analyses of four samples showing the hydrogen isotope data acquired at the beginning (red circles) and at the end of the long-term run (blue dots).

Software-controlled intermediate H3+ factor determinations after every 40 injections guarantee stability even if analytical conditions, such as water background variations from carrier gas supply, vary. The H3+ factor value was at 4.2 ppm/nA.

An example of ethanol and USGS46 (water standard) in Figure 4 demonstrates stability of hydrogen isotope data over the entire sequence.

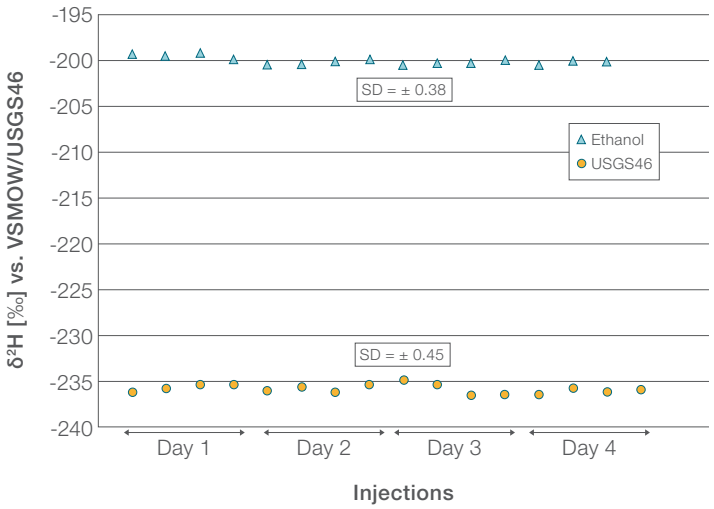

Figure 4. Stability of hydrogen isotope delta value for two different samples over a period of 4 days. Each data point is an average of 10 injections (N=10). The given standard deviation is related to the average values displayed.

Conclusions

Implementation of Cr reactor filling is quick and easy, allowing for improved data quality of hydrogen analysis of S/N/halogens bearing samples. Cr granules can be purchased separately as well as the inner quartz tube, offering a cost-effective solution. Packing heights and instrumental setup remain identical except for the reduced reactor operating temperature.

Literature

1. Kelly S. D., K. D. Heaton, P. Brereton (2001): Deuterium/hydrogen isotope ratio measurement of water and organic samples by continuous-flow isotope ratio mass spectrometry using chromium as the reducing agent in an elemental analyser. Rapid Commun. Mass Spectrom. (15), p. 1283-1286.
2. Morrison J., T. Brockwell, T. Merren, F. Fourel, A. M. Phillips (2001): On-Line High-Precision Stable Hydrogen Isotopic Analyses on Nanoliter Water Samples. Anal. Chem. (73), p. 3570-3575.
3. Hunsinger G. B., C. A. Tipple, L. A. Stern (2013): Gaseous byproducts from high-temperature thermal conversion elemental analysis of nitrogen- and sulfur-bearing compounds with considerations for δ^2H and $\delta^{18}O$ analyses. Rapid Commun. Mass Spectrom. (27), p. 1649–1659.
4. Meier-Augenstein W., H. F. Kemp, C. M. Lock (2009): N_2: a potential pitfall for bulk ^2H isotope analysis of explosives and other nitrogen-rich compounds by continuous-flow isotope-ratio mass spectrometry. Rapid Commun. Mass Spectrom. (23), p. 2011-2016.
5. Gehre M., J. Renpenning, T. Gilevska, H. Qi, T. B. Coplen, H. A. J. Meijer, W. A. Brand, A. Schimmelmann (2015): On-Line Hydrogen-Isotope Measurements of Organic Samples Using Elemental Chromium: An Extension for High Temperature Elemental-Analyzer Techniques. Anal. Chem. (87), p. 5198–5205.
6. Renpenning J., S. Kümmel, K. L. Hitzfeld, A. Schimmelmann, M. Gehre (2015): Compound-Specific Hydrogen Isotope Analysis of Heteroatom-Bearing Compounds via Gas Chromatography–Chromium-Based High-Temperature Conversion (Cr/HTC)–Isotope Ratio Mass Spectrometry. Anal. Chem. (87), p. 9443–9450.

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