APPLICATION NOTE

EA-IRMS: Fast and Precise Isotope Analysis of Liquids on a Delta V Isotope Ratio MS with a High Temperature Conversion Elemental Analyzer

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Key Words
EA-IRMS, Isotope Ratio MS, TC/EA, Water Analysis

Introduction

^{18}O and ^{2}H isotope ratio analysis of aqueous solutions such as water, urine, blood plasma, wine, can be performed by a variety of different techniques: equilibration, chromium reduction and carbon reduction (also referred to as high temperature conversion or pyrolysis). The high temperature conversion (TC) method allows a direct isotope ratio analysis of both oxygen and hydrogen in continuous flow mode. It offers the analysis of two isotopes in five minutes from only one injection of water samples as small as 0.1 µL.

Analytical Method

High temperature conversion in continuous flow mode became available with the introduction of the glassy carbon reactors. The conversion is based on the reaction:

$$H_2O + C \rightarrow H_2 + CO^1$$

Water samples are entrained in a He carrier gas stream and passed through a glassy carbon reactor at 1400 °C. The tube-in-tube principle (glassy carbon tube in a ceramic tube, Figure 1) prevents oxidation of the glassy carbon by keeping the tube in an oxygen-free atmosphere, constantly flushed by a flow of He.

Contamination or exchange of the O in the sample CO with O in the surrounding ceramic (Al_2O_3) tube is prevented because the reaction takes place inside the glassy carbon tube.

Isotope Ratio Analysis of Aqueous Solutions, e.g.

- Water
- Waste water
- Beer
- Wine
- Fruit juice
- Urine
- Blood plasma
- Ice
- Atmospheric water

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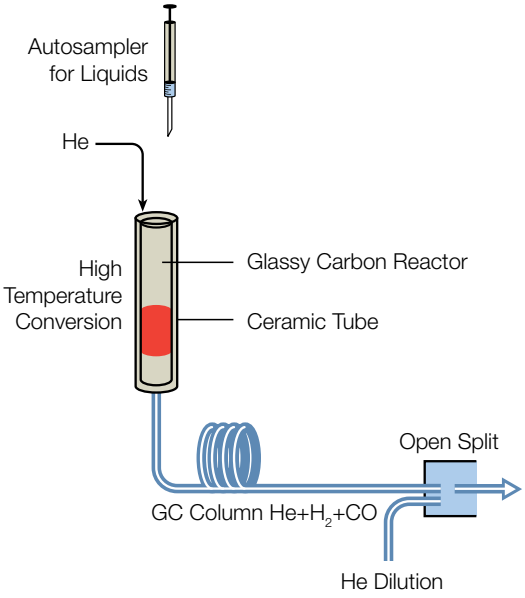

Figure 1. Schematic of the Thermo Scientific high temperature conversion elemental analyzer.

The products of the reduction reaction, H_2 and CO, are separated on a gas chromatographic column and analyzed directly in a Thermo Scientific™ Delta™ V Isotope Ratio Mass Spectrometer. After collecting the ion beams of *m/z* 2 and *m/z* 3 in the H_2 peak a fast switch of the magnetic field allows the subsequent collection of *m/z* 28 and *m/z* 30 in the CO peak (dual measurement mode). A narrow stainless steel insert is used at the top of the reactor to ensure both rapid and low memory transfer of the water into the hot zone. The system settings are given in Table 1 and 2.

It is essential that the injection of the water sample takes place immediately after the needle penetrates the septum to avoid isotopic fractionation resulting from evaporation in the needle tip. After the sample injection, the needle stays in the hot reactor for a certain period of time in order to remove any sample residue prior to the next injection.

Table 1. High temperature conversion elemental analyzer (TC/EA) settings for H and O isotope ratio analysis.

Analytical Conditions	
Reactor Temperature	1400 °C
GC Oven Temperature	100 °C
Carrier Flow	100 ml/min
Autosampler Type	Thermo Scientific AS 3000
Syringe Size	0.5 µL

Table 2. AS 3000 Autosampler settings.

Analytical Conditions	
Injection Volume	0.1 µL
Plunger Strokes	3
Rinses	0
Pre-Injection Dwell Time	0 s
Post-Injection Dwell Time	16 s
Solvent Wash Cycle	0

Results

Accuracy

Table 3 shows data from an installation of a TC/EA at a customer site. International water standards (IAEA, Vienna) plus a lab standard (Sample A) were injected in the given sequence. The water standards cover the full range of δ^2H and $\delta^{18}O$ values of natural water. The specifications of the TC/EA are < 2‰ for δ^2H and < 0.2‰ for $\delta^{18}O$. The typical precision achieved during routine analysis can be < 1‰ for δ^2H and < 0.1‰ for $\delta^{18}O$. All samples were analyzed in dual measurement mode.

The uncorrected raw data in Table 3 show that there is no need for any post-acquisition evaluation or correction. The direct conversion of the sample in the reactor, together with a highly precise, small and stable H^{3+}-factor of 6.2 ppm/nA provides very accurate delta values. This is a clear advantage over equilibration techniques. Common approaches for post-evaluation of raw delta values like the SMOW/SLAP scaling and drift corrections have been discussed by several authors.[2, 3, 4]

Memory

In Table 3 only the first data point of each set of five injections shows the influence of preceding samples. Large differences between delta values of adjacent samples can corrupt the first analysis due to memory effects mainly caused by the syringe. The implementation of post-injection dwell time of the syringe in the reactor removes most of this memory. Washing cycles for the syringe do not help here because any solvent would contaminate the syringe with H- and O-isotopes.

The data presented in Figure 2, Figure 3, Table 3, Table 4 and Table 5 are not warranted because they exceed product specifications. The warranted product specifications for δ^2H is ±2‰ (1 sd) measured on 0.5 µl of water and for $\delta^{18}O$ is ±0.2‰ (1 sd) measured on 0.5 µl of water.

Table 3. Mean and Standard Deviation (S.D.) of δ^2H and $\delta^{18}O$ values of five consecutive injections of international water standards GISP, SLAP, SMOW and a lab standard. The data is given in sequence of injection to demonstrate memory effects. The table shows raw data and data after scaling with SMOW and SLAP. The data was acquired during field installation. Strike-through data is not considered.

	δ^2H [‰] Raw	Mean	S.D.	δ^2H [‰] After Scaling	IAEA Accepted Value	$\delta^{18}O$ [‰] Raw	Mean	S.D.	$\delta^{18}O$ [‰] After Scaling	IAEA Accepted Value
GISP	~~185.03~~					~~24.23~~				
	-186.95					-24.67				
	-186.37					-24.75				
	-187.09					-24.75				
	-186.62	-186.76	0.32	-188.99	-189.5	-24.84	-24.75	0.07	-24.73	-24.5
SLAP	~~-420.53~~					~~-55.16~~				
	-422.13					-55.36				
	-422.35					-55.42				
	-424.45					-55.89				
	-422.67	-422.90	1.06	-428.00	-428.0	-55.52	-55.54	0.24	-55.50	-55.5
SMOW	~~-1.76~~					~~-0.32~~				
	-0.29					-0.04				
	0.31					-0.06				
	-0.02					-0.02				
	-0.11	-0.03	0.25	0.00	0.0	0.13	0.01	0.09	0.00	0.0
Sample A	~~-47.10~~					~~-7.44~~				
	-42.47					-6.99				
	-41.40					-6.82				
	-41.32					-6.66				
	-40.11	-41.32	0.96	-41.79	–	-6.76	-6.81	0.14	-6.81	–

Analysis Time

Table 4 shows a sequence of injections with samples of Antarctic precipitation with similar isotope ratio values Mean and Standard Deviation (S.D.) were calculated from five consecutive injections per sample. The mean precision for δ^2H is << 0.6‰ which is a requirement for ice core analysis by paleoclimatologists. High resolution data of long ice cores demand high sample throughput.

Figure 2 and Figure 3 compare the mean value with the first injection of each set to see if the number of repetitions can be reduced without affecting the accuracy. All $\delta^{18}O$ isotope values of the first injection fall within the S.D. except for Sample H showing that already the first injection gives correct results. About half of the δ^2H values of the first injection fall outside the S.D. range requiring repetition.

Table 4. Mean and Standard Deviation (S.D.) of δ^2H and $\delta^{18}O$ values of five consecutive sample injections (N = 5) with similar isotope ratio values. No data was excluded as memory effects are negligible. Standard: N = 3.

Sample	Mean δ^2H	S.D.	Mean $\delta^{18}O$	S.D.
Standard	-413.82	0.40	-39.48	0.07
Sample A	-429.78	0.43	-41.46	0.03
Sample B	-423.93	0.79	-40.68	0.09
Sample C	-422.30	0.55	-40.52	0.08
Sample D	-418.52	0.55	-40.02	0.06
Standard	-414.56	0.28	-39.58	0.11
Sample E	-402.63	0.48	-37.94	0.04
Sample F	-398.87	0.25	-37.54	0.08
Sample G	-392.22	0.88	-36.56	0.25
Sample H	-394.69	0.48	-36.83	0.13
Standard	-412.87	0.76	-39.15	0.13

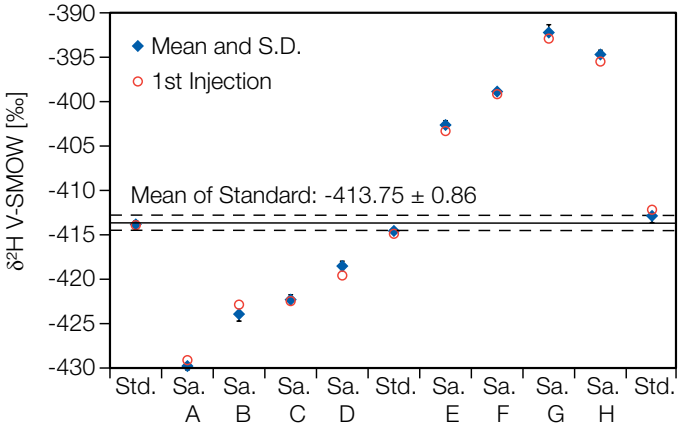

Figure 2. δ²H mean (sample N = 5, Standard N = 3) with Standard Deviation. Red circle data points represent the first injection of each set, all first injections fall within the S.D. range except for Sample H.

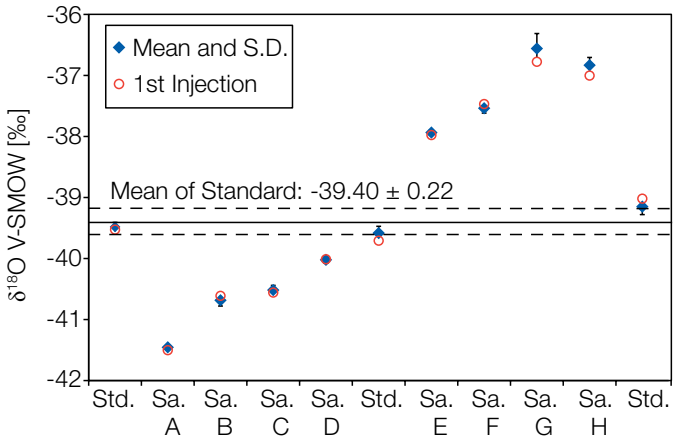

Figure 3. δ¹⁸O mean (sample N = 5, standard N = 3) with Standard Deviation. Red circle data points represent the first injection of each set. Most first injections fall within the S.D. range.

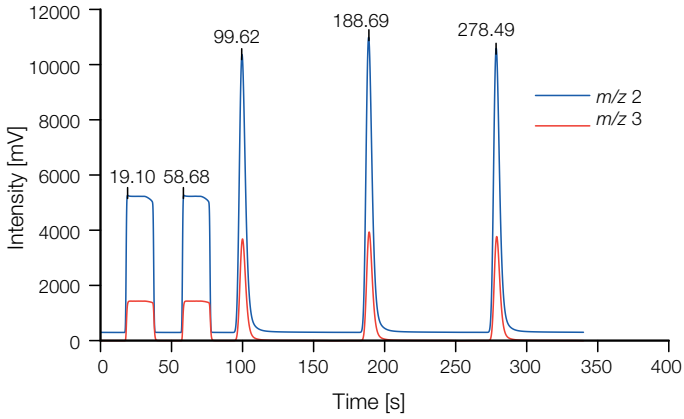

Figure 4. Single measurement δ²H with multiple injections of the same sample to account for two repetitions. The analysis time is six minutes.

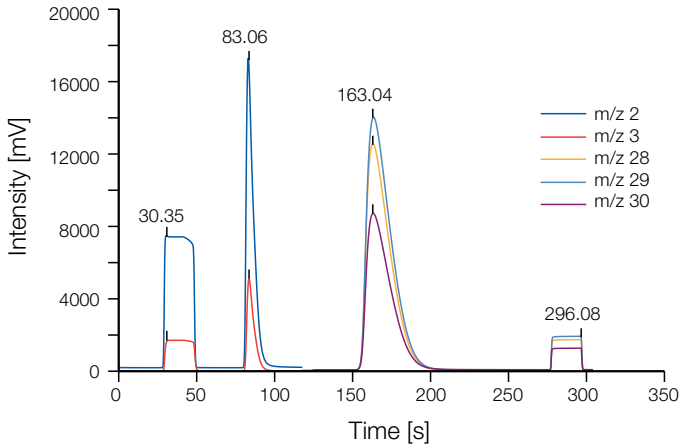

Figure 5. Dual measurement of δ²H and δ¹⁸O from a single injection with a fast magnet switch at 120 s. The analysis time can be reduced to less than five minutes.

In Short

Single Measurement δ¹⁸O

6 minutes analysis time,
no repetitions for screening required (N = 1),
10 injection per hour,
240 samples per day

Single Measurement δ²H

6-7 minutes analysis time,
2 repetitions (multiple injections, N = 3),
9 samples per hour,
216 samples per day
See Figure 4

Dual Measurement δ²H and δ¹⁸O

5-6 minutes analysis time,
2 repetitions (N = 3),
9 injections per hour,
72 samples per day
(9 injections x 24 h/3(triplicate) = 72)
See Figure 5

Table 5. Mean and Standard Deviation (S.D.) of δ²H and δ¹⁸O values of two standards and ethanol demonstrating the possibility to run organic liquids. N = 10 for standards, N = 5 for ethanol.

Sample	Mean δ²H	S.D.	Mean δ¹⁸O	S.D.
Lab Standard	-53.69	0.20	-7.84	0.04
V-SMOW	0.00	0.34	0.00	0.08
GISP	-189.50	0.40	-24.80	0.05
Ethanol	-234.80	0.12	-24.18	0.08
Lab Standard	-53.76	0.39	-7.85	0.03

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Other Liquid Samples

While isotope ratio analysis of water is by far the predominant application, other substrates have been tested, including purified blood plasma, urine, and ethanol (see Table 5), see also Calderone et al. for ethanol applications.[5] The application lab of Thermo Fisher Scientific™, Bremen, Germany, took part in an interlaboratory study, the object of which was to evaluate the use of tetramethylurea (TMU) as a reference compound for TC/EA-IRMS analysis of wine and alcohols as defined in European Commission Regulation (EEC) N° 2676/90.

The final report of the TC/EA-IRMS interlaboratory study states the applicability and emerging potential of EA-IRMS for food authenticity testing.[6] Even the analysis of organic substances like dodecane, methyl dodecanoate and methyl N-methylanthranilate produced good results.

Conclusion

Since its introduction in 1997, the Thermo Scientific high temperature conversion elemental analyzer TC/EA has created a new field of application for the O- and H-isotope analysis world-wide. TC/EA-IRMS is since then used for the analysis of liquids.

The advantage of fast sub-µL analysis of liquid samples (only five minutes for two isotope ratios) by far outweighs the eventually lower precision.

Low investment with high sample throughput leads to low cost per analysis. In addition, an autosampler for solids with minor modifications on the reactor packing makes the TC/EA also a valuable system for the isotope ratio analysis of solid samples.

Since 2003, the oven design and reactor technology of the TC/EA has been integrated in the Thermo Scientific™ EA IsoLink™ IRMS System, so that Dumas combustion for the analysis of N, C and S isotopes is combined with high temperature conversion for analysis of O and H isotopes in a single system.

The EA IsoLink IRMS System enables the user to switch from N-C isotope ratio analysis to H-O isotope ratio analysis within just a few minutes. The performance of water analyses in both elemental analyzers the TC/EA and the EA IsoLink System are identical.

References and Related Literature

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