

THE HORIZON IRMS: HYDROGEN AND OXYGEN ANALYSIS BY IRMS

INTRODUCTION

Hydrogen and oxygen stable isotope measurements are applied routinely in application areas such as animal migration studies, food adulteration and hydrology.

This note describes the measurement of both O and H stable isotope ratios in a single analysis using high temperature pyrolysis coupled to a stable isotope ratio mass spectrometer.

δD and $\delta^{18}O$ results obtained from a Horizon IRMS interfaced to a HEKAtech high temperature oven will be shown. Analytical characteristics such as memory effects, accuracy and precision for both isotopes will be discussed.

Instrumentation

The Horizon IRMS from Nu Instruments is designed for flexibility, reliability and high performance operation, with user friendly instrument control and data analysis software. This next generation instrument possesses unique features for Continuous Flow (CF) analysis, interfacing to a wide range of sample preparation peripherals. The analyser is differentially pumped and incorporates Nu Instruments unique patented zoom optic system.

Experiment

A modified HEKAtech (HEKAtech GmbH) high temperature oven capable of reaching temperatures up to 1500°C was configured for OH operation and interfaced to the Horizon in CF mode. The modification consisted of the use of the so called bottom reactor fitting (IVA-Analysentechnik e.K), first described by Gehre et al who used it to purge the annular space between the inner and outer tubes and force all of the flow down the glassy carbon inner tube.

The setup in this method was modified after a suggestion (private communication) from Len Wasenaar² by which helium was allowed to enter the top of the reactor and split into two flows (figures 1 and 2). The first and main flow passes down the centre of the inner glassy carbon tube whilst the second and much smaller flow flushes the annular space between the glassy carbon and ceramic tubes. This flow 'typically set to 3-5 ml per minute' is controlled by a crimped vent on the bottom fitting. The advantage of using it in this way is that any CO generated by reaction between the glassy carbon and ceramic tubes is vented to atmosphere and so is virtually eliminated as a source of high backgrounds at mass 28, 29 and 30. Figure 3 shows the change in background mass 28 signal as a function of reactor temperature.

Samples dropped into the pyrolysis reactor of Figure 1 decompose to form H₂ and CO. These product gases then pass through the carbosorb trap which removes any so called "acid gases" that have been formed depending on sample composition. The H₂ and CO are separated spatially in time by the GC column, sampled by the open split interface, and analysed for isotopic composition by the Horizon IRMS.

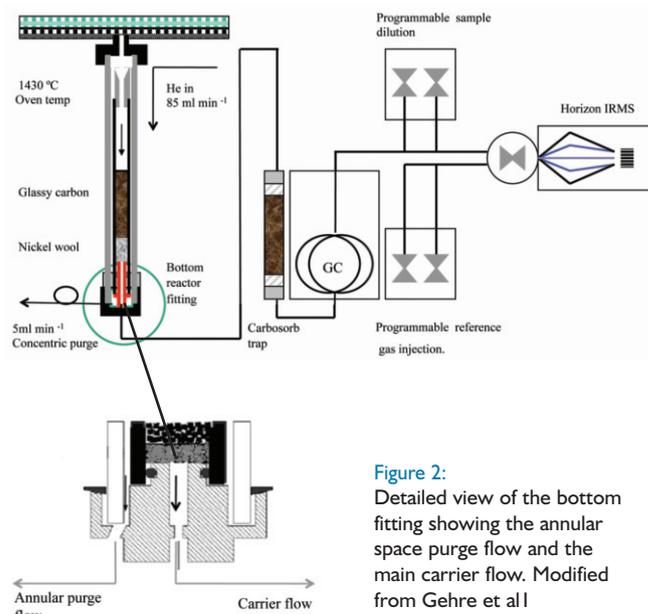
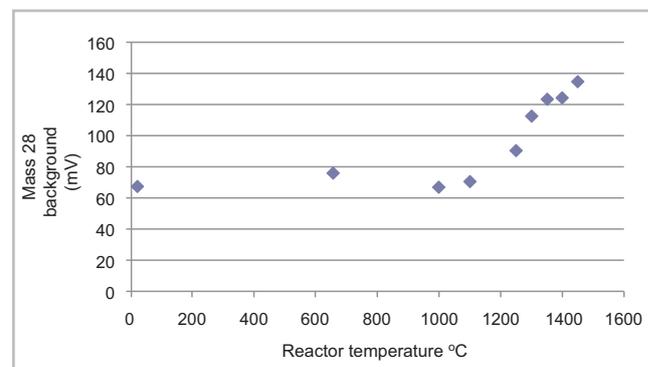


Figure 2: Detailed view of the bottom fitting showing the annular space purge flow and the main carrier flow. Modified from Gehre et al

Figure 3: Background versus temperature



Discussion

Solid standards calibrated for both ¹⁸O and ²H isotopes, in particular organic standards, are not readily available. To get around this a set of ¹⁸O calibrated inorganic standards comprising USGS-34, USGS-35 and IAEA-NO3 were used in conjunction with the IAEA ²H standard IAEA-CH-7 to generate a compound standard for both ¹⁸O and ²H isotopes. Samples of the ¹⁸O std were weighed into silver cups to which a weighed sample of CH-7 was then added. Whilst this provided all the necessary information required to produce a three point ¹⁸O calibration curve only one value for hydrogen was generated. A secondary lab standard (lycopodium powder) previously calibrated for δ^2H was obtained³ and used to generate a second ²H value.

A sample with an elevated ^2H value⁴ was added to the sample batch to provide some information on hydrogen inter-sample memory effects.

Prepared samples were loaded onto the carousel of a Vector SAS 80 position autosampler (EuroVector Milan) and sequentially pyrolysed by the HEKAtech high temperature oven. The integrated sample peak areas were compared isotopically to reference gas peaks introduced into the Horizon ion source by the fully programmable reference gas injection system.

Figure 4 shows a typical chromatogram obtained for the full analytical cycle of a single sample. It shows the IRMS output of the reference and sample peaks of H_2 followed by the reference and sample peaks of CO .

Automatic peak centring for both H_2 and CO is available if the user wishes, so ensuring optimal analysis conditions for each sample. At the start of the analysis the user may define automatic peak centring for none, all, or every n^{th} sample. The peak centre routine takes 20 seconds in total. Analytical results are shown in Tables 1 and 2.

Figure 4: Analysis chromatogram showing H_2 and CO generated from a single sample.

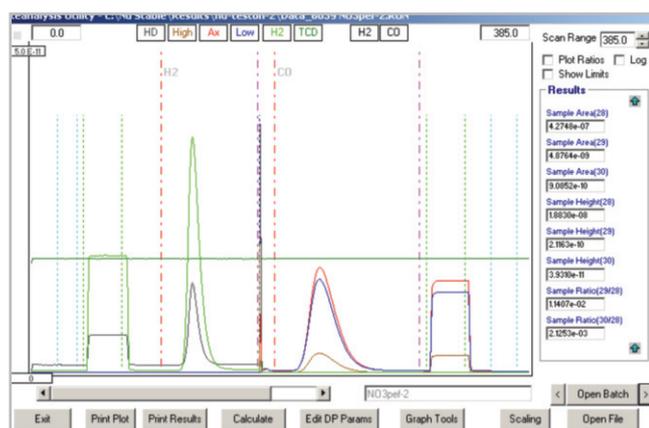


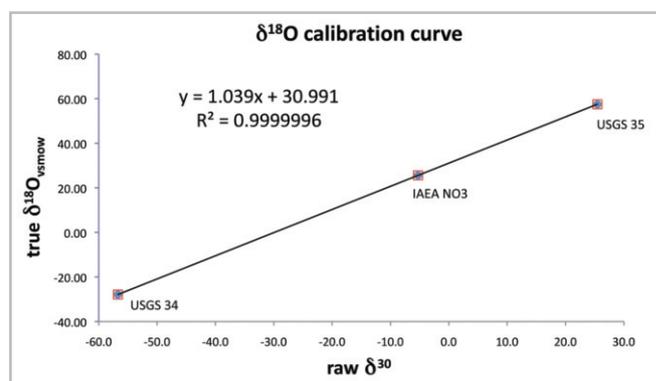
Table 1: Slope and Intercept data for hydrogen standards

STANDARD	raw δD	$\delta\text{D}_{\text{vsmow}}$
IAEA CH7	-115.29	-100
LYCOPODIUM	-167.62	-156
Slope	1.07	
Intercept	23.39	

Table 2: δD and $\delta^{18}\text{O}$ results for standards and samples. Note: *Inter sample memory effect on hydrogen resulting in first sample result being discarded. No memory effect was observed for oxygen analysis.

SAMPLE	$\delta\text{D}_{\text{vsmow}}$	1σ	n	$\delta^{18}\text{O}_{\text{vsmow}}$	1σ	n
CH7 + USGS 34	-99.4	1.4	6	-27.94	0.07	6
CH7 + IAEA NO3	-100.1	1.9	6	25.5	0.07	6
CH7 + USGS 35	-100.6	1.6	6	57.44	0.17	6
Lycopodium	-156.0	0.4	4*	20.21	0.12	5
AABenzoic	-85.0	1.1	28	24.81	0.08	28
AGBenzoic	+174.3	2.4	4*	19.81	0.07	5
Anthraquinone	-79.2	0.2	4*	19.16	0.08	5

Figure 5: ^{18}O calibration curve for oxygen standards



Conclusions

A Nu Instruments Horizon IRMS, interfaced to a HEKAtech high temperature oven fitted with a zero blank Vector SAS, 80 position autosampler were used to produce the data set of Figure 5. Both hydrogen ^2H and oxygen ^{18}O analyses were obtained from a single analysis of solid samples and the results show excellent precision and accuracy for both δD and $\delta^{18}\text{O}$. The total analysis time for each sample was < 7 minutes.

Memory effects

For this data set hydrogen measurements exhibited an inter-sample memory effect of magnitude 6% so that for sequential samples that are significantly different isotopically, the first measurement may have to be discarded. No memory effect associated with the oxygen analysis was observed.

Modified bottom reactor fitting

A novel application of a modified bottom reactor fitting in crimped purge flow operation has been described. By purging the annular space between the outer aluminium oxide and inner glassy carbon tubes the background CO is eliminated so removing an important analytical complication of the pyrolysis technique at elevated (1500°C) temperature.

Acknowledgements

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1. M. Gehre, H. Geilmann, J. Richter, R. A. Werner, W. A. Brand Continuous flow $^2\text{H}/1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ analysis of water samples with dual inlet precision: Rapid communications in mass spectrometry; Volume 18 Issue 22, Pages 2650 - 2660.

2. Len Wassenaar and Geoff Koehler (NHRC Saskatoon) Private communication suggesting the bottom reactor configuration used in this analysis.

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