High Precision Continuous Flow δ^{2}H and δ^{18}O Analysis of Water Samples

Jürgen M. Richter and Willi A. Brand

Background

On-line determination of δ^{2}H as well as δ^{18}O values from organic sample material using temperatures above 1300°C, a He carrier gas and a pool of carbon in the reaction zone has found growing interest. H- and O-containing organic material and some inorganic oxides react to H_2 and CO which are separated on a gas chromatograph and introduced into an isotope ratio mass spectrometer (IRMS).

The technique has proven successful mainly because other classical (dual inlet) means of determining δ^{2}H or δ^{18}O material are more tedious or more erroneous. Classical reduction techniques with U, Zn or Cr to measure ^{2}H/^{1}H in water with dual inlet techniques produce robust and reliable results, but require a special laboratory for measurements. On the other hand, precision of the ConFlo technique in particular for δ^{18}O values has remained an issue, mainly because of memory effects. Measurements could be made at the 0.2–0.3 ‰ level at best, which is not acceptable for water samples.

Objectives

The main objectives of the current experiments were:

- to develop a routine laboratory method for stable isotope ratio analysis of water samples
- to improve the measurement precision by reducing the sample-to-sample memory

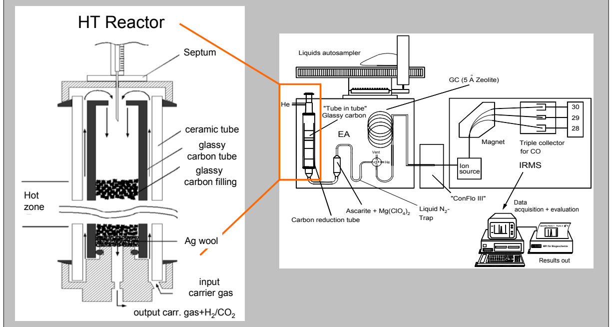


Figure 1: Left) Modifications to the high-temperature reactor (see text). **Right)** Scheme of the EA/IRMS coupling used for the "carbon reduction" method. The liquid N_2 trap is not active in case of measuring δ^{18}O- and δ^{2}H-values of aqueous samples.

Experimental Setup

We have modified the original setup of a high-temperature reactor (TC/EA) coupled on-line via a ConFlo III interface to a Delta$^+$XL IRMS (all units from Finnigan MAT). Water is injected automatically with an A200S autosampler equipped with a gas-tight syringe. Injection of 1.0 µL water is made with two washing cycles and five pullups. The needle is left in the externally heated septum for 16 s. In order to deposit waste water the needle tip is brought into contact with filter paper inside the waste bottle.

Changes to the reactor design

Major modifications to the original system (Fig. 1):

- changes to the design of the inner glassy carbon tube
- redirection of the carrier gas flow

The original open-ended glassy carbon tube was replaced with a longer one that is closed at the top end and extends over the whole length of the outer Al_2O_3 tube. A centered 2 mm hole was drilled into the closed side.

Instead of feeding the carrier gas into the tube at the septum head, we have attached the carrier line to the new bottom connector. By sealing the glassy carbon internally using a silicone O-ring (see lower part of Fig. 1) we force the carrier gas to pass first through the outer ring space between the Al_2O_3 tube and the glassy carbon tube. At the top, helium enters through the small hole in the glassy carbon reactor cover. Due to the high linear velocity of the carrier gas through this hole, water flash evaporating from the syringe cannot escape to the top. Thus, the glassy carbon is the only wetted surface the sample water can come into contact with. This design improves the sample-to-sample memory considerably (mostly < 2). After modifying the glassy carbon tube setup, also the yield has stabilized with a variablility of less than 5%.

Results

- By modifying the experimental setup, precision for δ^{18}O consistently improved to the 0.1 ‰ level.
- Memory effects within the high temperature reactor were reduced by avoiding over-spilling of evaporating water.
- Residual memory effects are corrected during post analysis evaluation (Tab. 1, Fig. 2). Memory correction considers up to eight measurements preceding the actual sample; the effect is most pronounced after a jump in isotopic composition. After manual selection of representative lab reference water injections, a usually small drift correction (=long-term memory) is applied. By comparing the reference value for our www-j1 standard with the drift-corrected value, the offset can be determined and subsequently corrected. Finally, values are scaled to the known difference between VSMOW and SLAP.

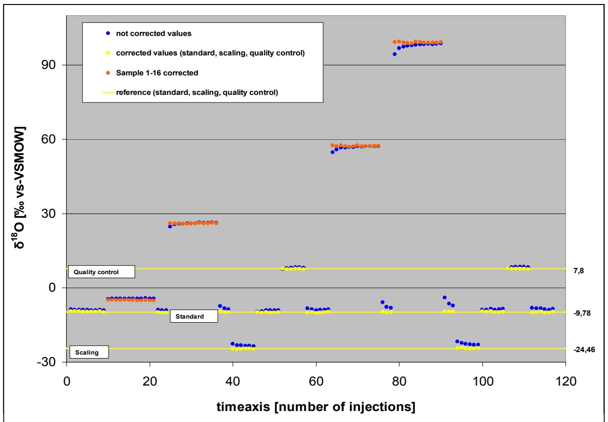
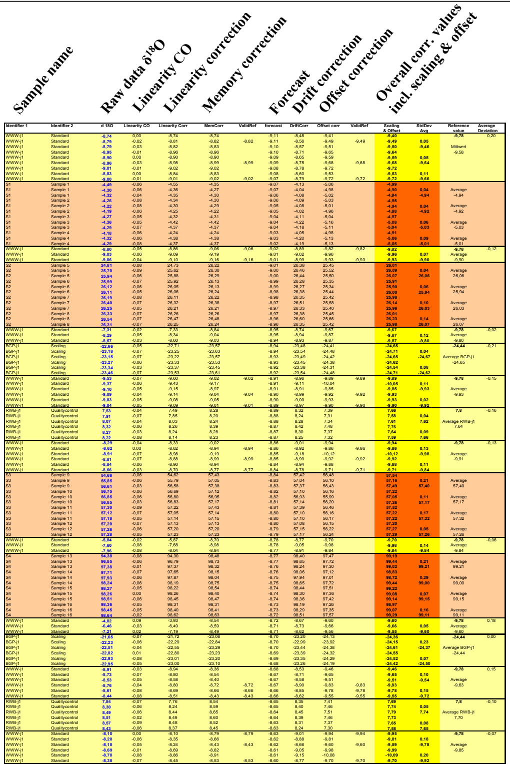


Figure 2: Comparison of uncorrected and corrected measurement values.



Sample name		Raw data δ^{18}O	Linearity CO	Linearity correction	Memory correction		Forecast	Drift correction	Offset correction		Overall corr. values incl. scaling & offset			
Identifier 1	Identifier 2	d 18O	Linearity CO	Linearity Corr	MemCorr	ValidRef	forecast	DriftCorr	Offset corr	ValidRef	Scaling & Offset	StdDev Avg	Reference value	Average Deviation
WWW-j1	Standard	-8,74	0,00	-8,74	-8,74		-9,11	-8,48	-9,41		-9,40		-9,78	0,20
WWW-j1	Standard	-8,79	-0,02	-8,81	-8,82	-8,82	-9,11	-8,56	-9,49	-9,49	-9,49	0,05		
WWW-j1	Standard	-8,79	-0,03	-8,82	-8,83		-9,10	-8,57	-9,51		-9,50	-9,46	Mittwert	
WWW-j1	Standard	-8,95	-0,01	-8,96	-8,96		-9,10	-8,71	-9,65		-9,64		-9,58	
WWW-j1	Standard	-8,90	0,00	-8,90	-8,90		-9,09	-8,65	-9,59		-9,59	0,05		
WWW-j1	Standard	-8,96	-0,03	-8,98	-8,99	-8,99	-9,09	-8,75	-9,68	-9,68	-9,68	-9,64		
WWW-j1	Standard	-9,01	-0,01	-9,02	-9,02		-9,08	-8,78	-9,72		-9,72			
WWW-j1	Standard	-8,83	0,00	-8,84	-8,83		-9,08	-8,60	-9,53		-9,53	0,11		
WWW-j1	Standard	-9,00	-0,01	-9,01	-9,02	-9,02	-9,07	-8,79	-9,72	-9,72	-9,72	-9,66		
S1	Sample 1	-4,49	-0,06	-4,55	-4,35		-9,07	-4,13	-5,06		-4,99			
S1	Sample 1	-4,30	-0,06	-4,36	-4,27		-9,07	-4,04	-4,98		-4,90	0,04	Average	
S1	Sample 1	-4,32	-0,04	-4,35	-4,30		-9,06	-4,08	-5,02		-4,94	-4,94	-4,94	
S1	Sample 2	-4,26	-0,08	-4,34	-4,30		-9,06	-4,09	-5,03		-4,95			
S1	Sample 2	-4,22	-0,08	-4,30	-4,29		-9,05	-4,08	-5,01		-4,94	0,04	Average	
S1	Sample 2	-4,19	-0,06	-4,25	-4,22		-9,05	-4,02	-4,96		-4,88	-4,92	-4,92	
S1	Sample 3	-4,27	-0,05	-4,32	-4,31		-9,04	-4,11	-5,04		-4,97			
S1	Sample 3	-4,36	-0,05	-4,42	-4,42		-9,04	-4,22	-5,16		-5,08	0,06	Average	
S1	Sample 3	-4,29	-0,07	-4,37	-4,37		-9,04	-4,18	-5,11		-5,04	-5,03	-5,03	
S1	Sample 4	-4,18	-0,06	-4,24	-4,24		-9,03	-4,05	-4,98		-4,91			
S1	Sample 4	-4,32	-0,06	-4,38	-4,38		-9,03	-4,20	-5,13		-5,06	0,09	Average	
S1	Sample 4	-4,29	-0,08	-4,37	-4,37		-9,02	-4,19	-5,13		-5,05	-5,01	-5,01	
WWW-j1	Standard	-8,80	-0,05	-8,86	-9,06	-9,06	-9,02	-8,89	-9,82	-9,82	-9,82		-9,78	-0,12
WWW-j1	Standard	-9,03	-0,06	-9,09	-9,19		-9,01	-9,02	-9,96		-9,96	0,07	Average	
WWW-j1	Standard	-9,06	-0,04	-9,10	-9,16	-9,16	-9,01	-8,99	-9,93	-9,93	-9,93	-9,90	-9,90	
S2	Sample 5	24,81	-0,08	24,73	26,22		-9,01	26,38	25,45		26,01			
S2	Sample 5	25,70	-0,09	25,62	26,30		-9,00	26,46	25,52		26,09	0,04	Average	
S2	Sample 5	25,94	-0,06	25,88	26,29		-9,00	26,44	25,50		26,07	26,06	26,06	
S2	Sample 6	25,99	-0,07	25,92	26,13		-8,99	26,28	25,35		25,91			
S2	Sample 6	26,12	-0,06	26,05	26,13		-8,99	26,27	25,34		25,90	0,06	Average	
S2	Sample 6	26,11	-0,05	26,06	26,24		-8,98	26,38	25,44		26,00	25,94	25,94	
S2	Sample 7	26,19	-0,08	26,11	26,22		-8,98	26,35	25,42		25,98			
S2	Sample 7	26,40	-0,07	26,32	26,38		-8,97	26,51	25,58		26,14	0,10	Average	
S2	Sample 7	26,25	-0,05	26,21	26,21		-8,97	26,33	25,40		25,96	26,03	26,03	
S2	Sample 8	26,33	-0,07	26,26	26,26		-8,97	26,38	25,45		26,01			
S2	Sample 8	26,54	-0,07	26,47	26,48		-8,96	26,60	25,66		26,23	0,14	Average	
S2	Sample 8	26,31	-0,07	26,25	26,24		-8,96	26,35	25,42		25,98	26,07	26,07	
WWW-j1	Standard	-7,31	-0,02	-7,33	-8,84		-8,95	-8,74	-9,67		-9,67		-9,78	-0,02
WWW-j1	Standard	-8,29	-0,05	-8,34	-9,04		-8,95	-8,94	-9,87		-9,87	0,12	Average	
WWW-j1	Standard	-8,57	-0,03	-8,60	-9,03		-8,94	-8,93	-9,87		-9,87	-9,80	-9,80	
BGP-j1	Scaling	-22,66	-0,05	-22,71	-23,57		-8,94	-23,48	-24,41		-24,65		-24,44	-0,21
BGP-j1	Scaling	-23,18	-0,07	-23,25	-23,63		-8,94	-23,54	-24,48		-24,71	0,04		
BGP-j1	Scaling	-23,15	-0,07	-23,22	-23,57		-8,93	-23,49	-24,42		-24,65	-24,67	Average BGP-j1	
BGP-j1	Scaling	-23,27	-0,06	-23,33	-23,53		-8,93	-23,45	-24,38		-24,62		-24,65	
BGP-j1	Scaling	-23,34	-0,03	-23,37	-23,45		-8,92	-23,38	-24,31		-24,54	0,08		
BGP-j1	Scaling	-23,46	-0,07	-23,53	-23,61		-8,92	-23,54	-24,48		-24,71	-24,62		
WWW-j1	Standard	-9,53	-0,07	-9,60	-9,02	-9,02	-8,91	-8,96	-9,89	-9,89	-9,89		-9,78	-0,15
WWW-j1	Standard	-9,37	-0,06	-9,43	-9,17		-8,91	-9,11	-10,04		-10,05	0,11		
WWW-j1	Standard	-9,10	-0,05	-9,15	-8,97		-8,91	-8,91	-9,85		-9,85	-9,93	Average	
WWW-j1	Standard	-9,09	-0,04	-9,14	-9,04	-9,04	-8,90	-8,99	-9,92	-9,92	-9,93		-9,93	
WWW-j1	Standard	-9,03	-0,05	-9,08	-9,05		-8,90	-9,00	-9,93		-9,93	0,02		
WWW-j1	Standard	-9,04	-0,05	-9,09	-9,01	-9,01	-8,89	-8,97	-9,90	-9,90	-9,90	-9,92		
RWB-j1	Qualitycontrol	7,53	-0,04	7,49	8,28		-8,89	8,32	7,39		7,66		7,8	-0,16
RWB-j1	Qualitycontrol	7,91	-0,07	7,85	8,20		-8,88	8,24	7,31		7,58	0,04		
RWB-j1	Qualitycontrol	8,07	-0,04	8,03	8,24		-8,88	8,28	7,34		7,61	7,62	Average RWB-j1	
RWB-j1	Qualitycontrol	8,32	-0,06	8,26	8,39		-8,87	8,42	7,48		7,76		7,64	
RWB-j1	Qualitycontrol	8,27	-0,03	8,24	8,28		-8,87	8,30	7,37		7,64	0,09		
RWB-j1	Qualitycontrol	8,22	-0,08	8,14	8,23		-8,87	8,25	7,32		7,59	7,66		
WWW-j1	Standard	-8,29	-0,04	-8,33	-9,02		-8,86	-9,01	-9,94		-9,94		-9,78	-0,13
WWW-j1	Standard	-8,62	0,00	-8,62	-8,94	-8,94	-8,86	-8,92	-9,86	-9,86	-9,86	0,13		
WWW-j1	Standard	-8,91	-0,07	-8,98	-9,19		-8,85	-9,18	-10,12		-10,12	-9,98	Average	
WWW-j1	Standard	-8,81	-0,07	-8,88	-8,99	-8,99	-8,85	-8,99	-9,92	-9,92	-9,92		-9,91	
WWW-j1	Standard	-8,84	-0,06	-8,90	-8,94		-8,84	-8,94	-9,88		-9,88	0,11		
WWW-j1	Standard	-8,66	-0,03	-8,70	-8,77	-8,77	-8,84	-8,78	-9,71	-9,71	-9,71	-9,84		
S3	Sample 9	54,68	-0,06	54,62	57,43		-8,84	57,42	56,48		57,54			
S3	Sample 9	55,85	-0,06	55,79	57,05		-8,83	57,04	56,10		57,16	0,21	Average	
S3	Sample 9	56,61	-0,03	56,58	57,38		-8,83	57,37	56,43		57,49	57,40	57,40	
S3	Sample 10	56,75	-0,06	56,69	57,12		-8,82	57,10	56,16		57,22			
S3	Sample 10	56,85	-0,06	56,80	56,95		-8,82	56,93	55,99		57,05	0,11	Average	
S3	Sample 10	56,85	-0,03	56,83	57,17		-8,81	57,14	56,20		57,26	57,17	57,17	
S3	Sample 11	57,30	-0,09	57,22	57,43		-8,81	57,39	56,46		57,52			
S3	Sample 11	57,12	-0,07	57,05	57,14		-8,80	57,10	56,16		57,22	0,17	Average	
S3	Sample 11	57,18	-0,05	57,14	57,15		-8,80	57,10	56,17		57,22	57,32	57,32	
S3	Sample 12	57,20	-0,07	57,13	57,13		-8,80	57,08	56,15		57,20			
S3	Sample 12	57,26	-0,06	57,20	57,20		-8,79	57,15	56,22		57,27	0,05	Average	
S3	Sample 12	57,28	-0,05	57,23	57,23		-8,79	57,17	56,24		57,29	57,26	57,26	
WWW-j1	Standard	-5,84	-0,02	-5,87	-8,70		-8,78	-8,77	-9,70		-9,70		-9,78	-0,06
WWW-j1	Standard	-7,60	-0,08	-7,68	-8,98		-8,78	-9,05	-9,98		-9,98	0,14	Average	
WWW-j1	Standard	-7,96	-0,08	-8,04	-8,84		-8,77	-8,91	-9,84		-9,84	-9,84	-9,84	
S4	Sample 13	94,38	-0,08	94,30	98,48		-8,77	98,40	97,47		99,19			
S4	Sample 13	96,85	-0,06	96,79	98,73		-8,77	98,65	97,72		99,44	0,21	Average	
S4	Sample 13	97,38	-0,01	97,37	98,32		-8,76	98,24	97,30		99,02	99,21	99,21	
S4	Sample 14	97,71	-0,07	97,65	98,15		-8,76	98,06	97,12		98,83			
S4	Sample 14	97,93	-0,06	97,87	98,04		-8,75	97,94	97,01		98,72	0,39	Average	
S4	Sample 14	98,24	-0,06	98,19	98,75		-8,75	98,65	97,72		99,44	99,00	99,00	
S4	Sample 15	98,27	-0,05	98,22	98,54		-8,74	98,44	97,51		99,22			
S4	Sample 15	98,26	0,00	98,26	98,40		-8,74	98,30	97,36		99,08	0,07	Average	
S4	Sample 15	98,51	-0,06	98,45	98,47		-8,74	98,36	97,42		99,14	99,15	99,15	
S4	Sample 16	98,36	-0,05	98,31	98,31		-8,73	98,19	97,26		98,97			
S4	Sample 16	98,45	-0,05	98,40	98,41		-8,73	98,29	97,35		99,07	0,16	Average	
S4	Sample 16	98,64	-0,02	98,62	98,63		-8,72	98,51	97,57		99,29	99,11	99,11	
WWW-j1	Standard	-4,02	0,09	-3,93	-8,54		-8,72	-8,67	-9,60		-9,60		-9,78	0,18
WWW-j1	Standard	-6,46	-0,03	-6,49	-8,59		-8,71	-8,73	-9,66		-9,66	0,05	Average	
WWW-j1	Standard	-7,21	0,02	-7,19	-8,49		-8,71	-8,62	-9,56		-9,55	-9,60	-9,60	
BGP-j1	Scaling	-21,65	-0,07	-21,72	-23,06		-8,70	-23,20	-24,13		-24,36		-24,44	0,00
BGP-j1	Scaling	-22,23	-0,06	-22,29	-22,84		-8,70	-22,99	-23,92		-24,15	0,23		
BGP-j1	Scaling	-22,51	-0,04	-22,55	-23,29		-8,70	-23,44	-24,38		-24,61	-24,37	Average BGP-j1	
BGP-j1	Scaling	-22,82	0,01	-22,80	-23,23		-8,69	-23,39	-24,32		-24,55		-24,44	
BGP-j1	Scaling	-22,93	-0,08	-23,01	-23,20		-8,69	-23,35	-24,29		-24,52	0,07		
BGP-j1	Scaling	-22,95	-0,05	-23,00	-23,10		-8,68	-23,26	-24,19		-24,42	-24,50		
WWW-j1	Standard	-8,91	-0,03	-8,94	-8,36		-8,68	-8,53	-9,46		-9,46		-9,78	0,15
WWW-j1	Standard	-8,73	-0,07	-8,80	-8,54		-8,67	-8,71	-9,65		-9,65	0,10		
WWW-j1	Standard	-8,53	-0,05	-8,58	-8,40		-8,67	-8,58	-9,51		-9,51	-9,54	Average	
WWW-j1	Standard	-8,76	-0,04	-8,80	-8,72	-8,72	-8,67	-8,90	-9,83	-9,83	-9,83		-9,63	
WWW-j1	Standard	-8,61	-0,08	-8,69	-8,66	-8,66	-8,66	-8,85	-9,78	-9,78	-9,78	0,15		
WWW-j1	Standard	-8,44	-0,08	-8,51	-8,43	-8,43	-8,66	-8,62	-9,55	-9,55	-9,55	-9,72		
RWB-j1	Qualitycontrol	7,84	-0,07	7,76	8,54		-8,65	8,35	7,41		7,69		7,8	-0,10
RWB-j1	Qualitycontrol	8,30	-0,06	8,24	8,59		-8,65	8,40	7,46		7,74	0,05		
RWB-j1	Qualitycontrol	8,49	-0,06	8,44	8,65		-8,64	8,45	7,51		7,79	7,74	Average RWB-j1	
RWB-j1	Qualitycontrol	8,51	-0,02	8,49	8,60		-8,64	8,39	7,46		7,73		7,70	
RWB-j1	Qualitycontrol	8,57	-0,09	8,48	8,52		-8,63	8,31	7,37		7,65	0,08		
RWB-j1	Qualitycontrol	8,43	-0,06	8,37	8,45		-8,63	8,24	7,30		7,58	7,65		
WWW-j1	Standard	-8,10	0,00	-8,10	-8,79	-8,79	-8,63	-9,01	-9,94	-9,94	-9,95		-9,78	-0,07
WWW-j1	Standard	-8,28	-0,06	-8,35	-8,66		-8,62	-8,88	-9,81		-9,81	0,18		
WWW-j1	Standard	-8,18	-0,05	-8,24	-8,43	-8,43	-8,62	-8,66	-9,60	-9,60	-9,59	-9,78	Average	
WWW-j1	Standard	-8,69	-0,01	-8,69	-8,82		-8,61	-9,05	-9,98		-9,99		-9,85	
WWW-j1	Standard	-8,78	-0,08	-8,86	-8,91		-8,61	-9,15	-10,08		-10,09	0,20		
WWW-j1	Standard	-8,38	-0,07	-8,45	-8,53	-8,53	-8,60	-8,77	-9,70	-9,70	-9,70	-9,92		

Table 1: Example for post analysis evaluation of the measured δ^{18}O data (shortened extract of evaluation spreadsheet). Blue values represent uncorrected raw data, samples are high-lighted in red, standard, scaling and quality control are high-lighted in yellow.