Supporting Information

On-line Hydrogen-Isotope Measurements of Organic Samples Using Elemental Chromium: An Extension for High Temperature Elemental-Analyzer Techniques

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One important aspect of an analytical method is the conversion efficiency of an element in a sample to the sample gas. It is useful to measure the recovery (yield) of a reaction method.
For a better understanding of the chemical reaction, however, knowledge of the resulting byproducts is even more important. If significant products are formed that also contain the element of interest, this is likely to have impact on the accuracy of isotopic composition measurements and, thus, the accuracy of the results.

This supporting information shows details of reactions for both the HTC and the Cr-setups

Contents:

Table S-1: Between-sample memory test (Laboratory Leipzig, LSI)

Analysis sequence	**Sample**	**Raw data δ^2H / mUr**	**Outlier-corrected δ^2H / mUr (not calibrated)**	**Mean values and standard deviation / mUr**
1	vacuum oil, ^{2}H-enriched	405.4	405.4	
2		405.4	405.4	
3		406.5	406.5	
4		405.1	405.1	
5		408.9	408.9	**406.2** ± 1.6
6	water, IAEA 604	793.3		
7		800.8	800.8	
8		804.3	804.3	
9		803.6	803.6	
10		802.6	802.6	**802.8** ± 1.5
11	water, UC04	134.4		
12		124.4	124.4	
13		125.6	125.6	
14		122.6	122.6	
15		123.5	123.5	**124.2** ± 1.5
16	water, VSMOW2	12.9		
17		9.5	9.5	
18		10.5	10.5	
19		10.1	10.1	
20		8.6	8.6	**9.7** ± 0.8
21	water, SLAP2	–406.3		
22		–413.1	–413.1	
23		–414.9	–414.9	
24		–415.1	–415.1	
25		–415.2	–415.2	**–414.6** ± 1.0

The design of the reactor in the LSI shows a small memory between different samples. This is usually about 2 % of the difference between the previous and the following sample. Our daily routine ignores the first value of a new sample. The standard deviation is less than 2 mUr.

2. Considerations on backgrounds and/ or hydrogen-bearing byproducts of the HTC and Cr-EA techniques

2.1. Background of CHO-bearing compounds

Comparisons of the backgrounds and byproducts resulting from HTC-Pyrolysis (left) and Cr-EA (right) methods, H_2 yield for both methods ~100 %.

Figure S-1

HTC 1400 °C, helium 75 mL min^{-1}

IAEA-CH7 (polyethylene foil, C_2H_4)

Background: water-air

~30 µA (3 × 10^4 nA)

Background: water, nitrogen, oxygen

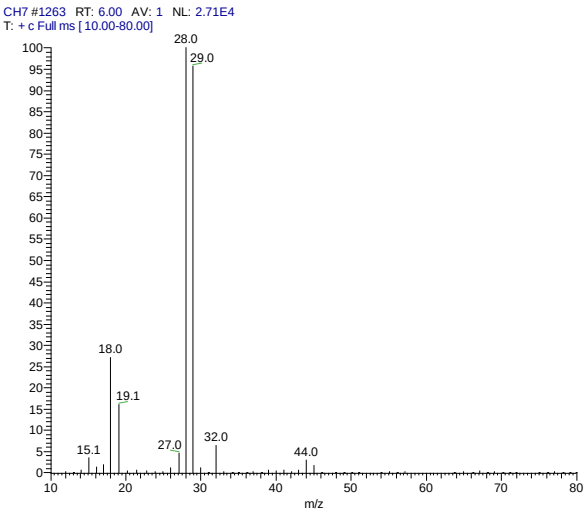
Figure S-2

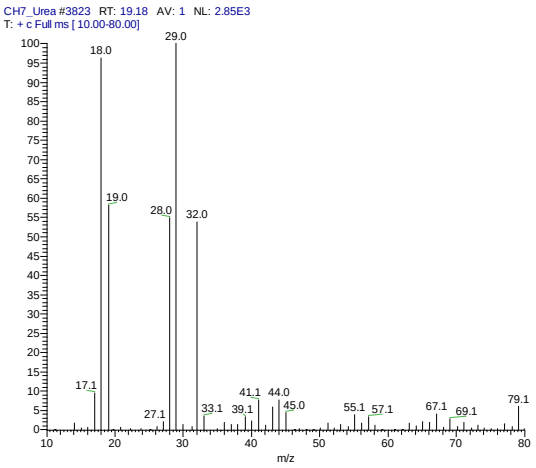
Cr-EA 1050 °C, helium 75 mL min^{-1}

Background: water-air

~3 µA (3 × 10^3 nA)

Background: water, nitrogen, oxygen





NBS 22 (Oil)

Figure S-3

HTC 1400 °C, helium 75 mL min^{-1}

[1]Background: water-air

~30 µA (3 × 10^4 nA)

Background: water, nitrogen, oxygen

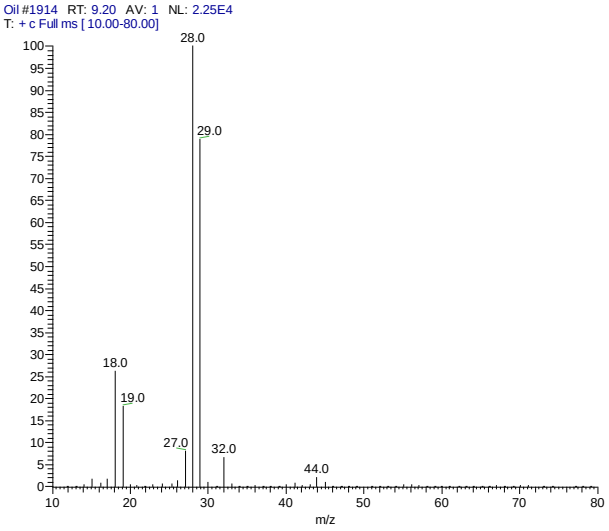
Figure S-4

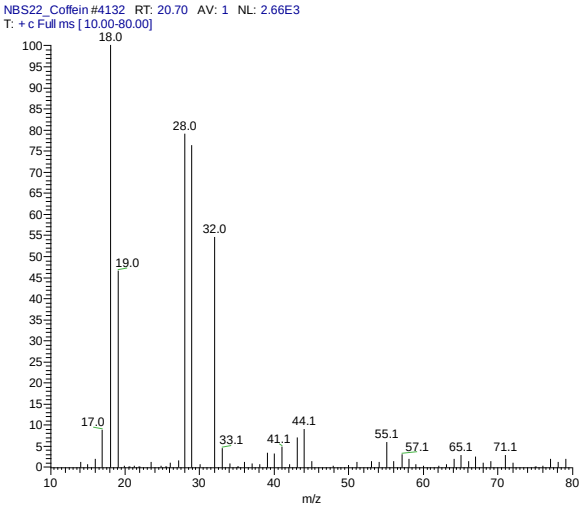
Cr-EA 1050 °C, helium 75 mL min^{-}

Background: water-air

~3 µA (3 × 10^3 nA)

Background: water, nitrogen, oxygen





2.2. Background of CHNO(S)-bearing compounds

Comparisons of the backgrounds and byproducts resulting from HTC-Pyrolysis (left) and Cr-EA (right) methods. The H_2 yield for HTC method is less than 100 %, depending on the compound. The H_2 yield for Cr-EA method is 100 %.

Cysteine (amino acid, $C_3H_7NO_2S$)

H_2 yield for HTC-method ~90 %

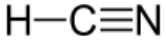
Figure S-5

HTC 1400 °C, helium 75 mL min^{-1}

[1]Background: HCN (m/z 27)

~2 mA (2 x 10^6 nA)

Byproduct: hydrogen cyanide, (nitrogen)



Formation of hydrogen bearing byproducts in addition to H_2

H_2 yield for Cr-EA method 100 %

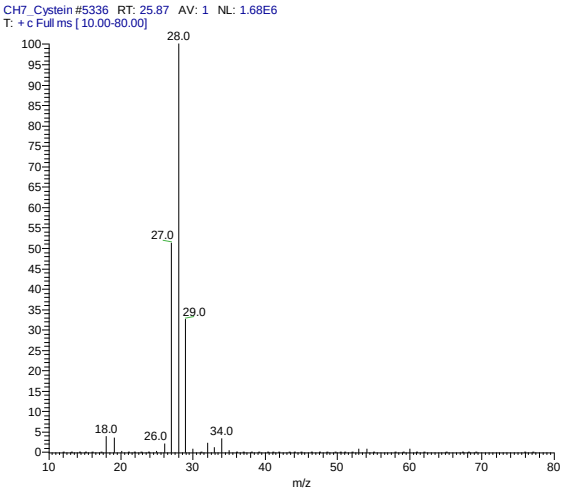
Figure S-6

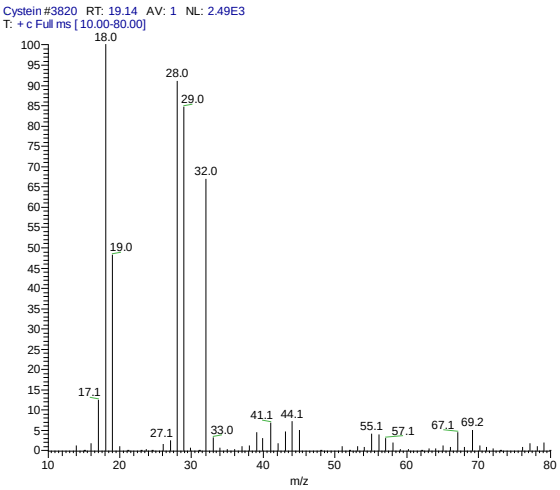
Cr-EA 1050 °C, helium 75 mL min^{-}

Background: water-air

~3 µA (3 x 10^3 nA)

Background: water, nitrogen, oxygen





Urea (CH_4N_2O)

H_2 yield for HTC-method ~90 %

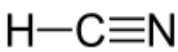
Figure S-7

HTC 1400 °C, helium 75 mL min^{-1}

Background: HCN (m/z 27)

~2 mA (2 x 10^6 nA)

Byproduct: hydrogen cyanide, (nitrogen)



Formation of hydrogen bearing byproducts in addition to H_2

H_2 yield for Cr-EA method 100 %

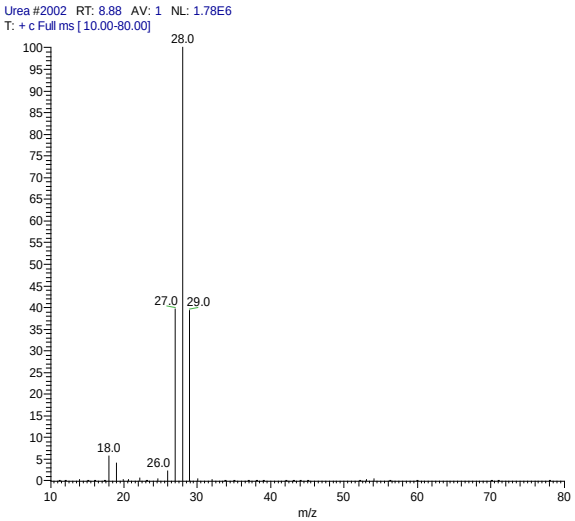
Figure S-8

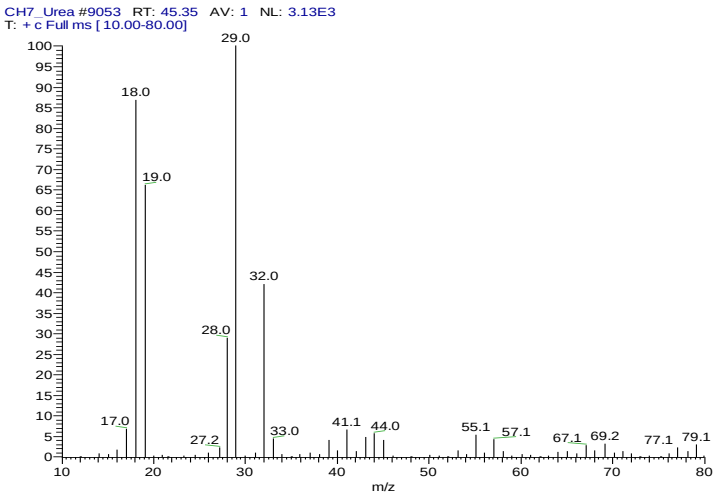
Cr-EA 1050 °C, helium 75 mL min^{-1}

Background: water-air

~3 µA (3 x 10^3 nA)

Background: water, nitrogen, oxygen



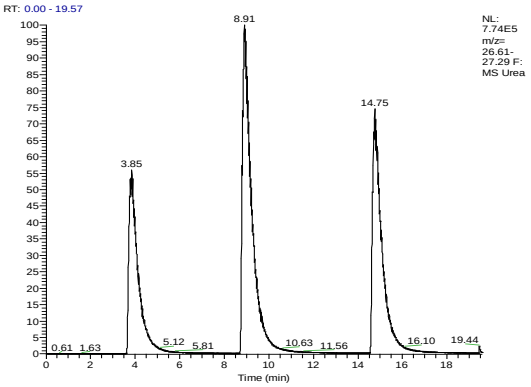


Mass selective Chromatogram of HCN from urea (mass 27)

H_2 yield for HTC-method ~90 %

Figure S-9

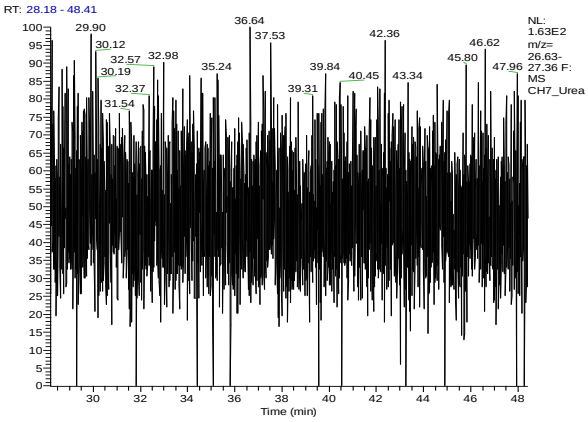
HTC 1400 °C, He 75 mL min^{-1}



H_2 yield for Cr-EA method 100 %

Figure S-10

Cr-EA 1050 °C, He 75 mL min^{-1}



2.3. Background of CHCl-containing compounds

Comparisons of the backgrounds and byproducts resulting from HTC-Pyrolysis (left) and Cr-EA (right) methods. The H_2 yield for HTC method is less than 100 %, depending on the compound. The H_2 yield for Cr-EA method is often less than 100 %, depending on the compound.
HCl formation as hydrogen bearing byproduct is observed. The differences in the intensity of HCl between the HTC- and the Cr-EA method are ~ factor 50

Figure S-11

HTC 1400 °C, helium 75 mL min^{-1}

DDT (dichlorodiphenyltrichlorethan, $C_{14}H_9Cl_5$)

H_2 yield for HTC-method ~90 %

Background: HCl (m/z 36)

~200 µA (2 x 10^5 nA)

Formation of hydrogen bearing byproducts in addition to H_2

Byproduct: hydrogen chloride

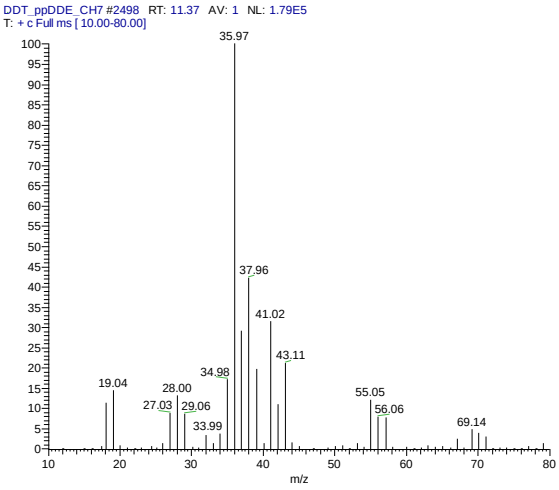


Figure S-12

Cr-EA 1050 °C, helium 75 mL min^{-1}

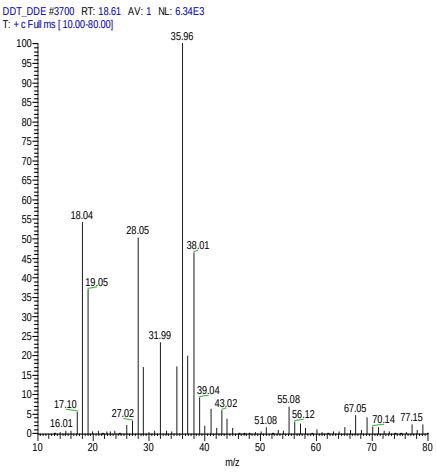
H_2 yield for Cr-EA method 98 %

Background: HCl (m/z 36)

~6 µA (6 x 10^3 nA)

Formation of hydrogen bearing by-products in addition to H_2

Main masses: hydrogen chloride, air



3. Observed effects in the isotopic measurement of water after analyzing a sequence of halogen-containing samples. Formation of hydrogen choride as a byproduct in addition to H_2 .

Hydrogen isotope data indicated the formation of HCl. Chlorine could have been released from hot chromium chloride via reaction with oxygen from water. A chlorine-containing Cr-reactor at high temperature seems to be problematic for routine isotopic measurements of water, especially when reference waters are used for isotopic calibration.

Figure S-13

Cr-EA 1050 °C, helium 75 mL min^{-1}

VSMOW2-reference water

Background: HCl (m/z 36)

~30 µA (3 x 10^4 nA)

Formation of hydrogen bearing byproducts in addition to H_2

Byproduct: hydrogen chloride

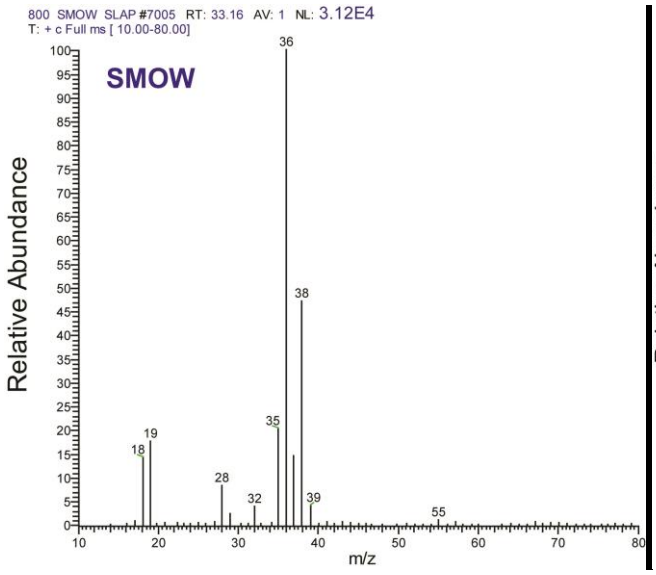


Figure S-14

Cr-EA 1050 °C, helium 75 mL min^{-1}

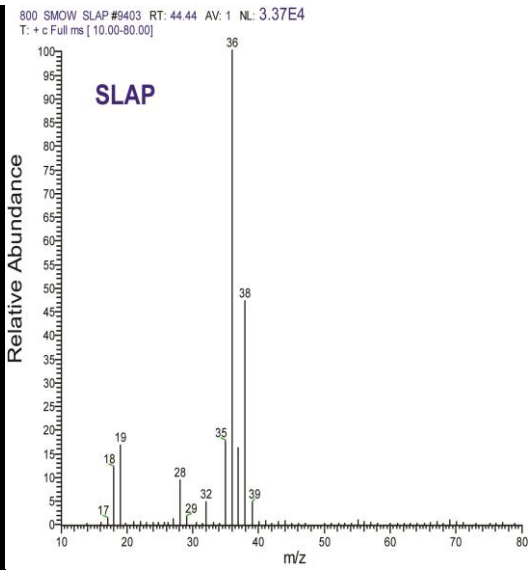
SLAP2-reference water

Background: HCl (m/z 36)

~30 µA (3 x 10^4 nA)

Formation of hydrogen bearing byproducts in addition to H_2

Byproduct: hydrogen chloride



The intensity of HCl is 10 x higher than the air-water background by the Cr-EA for water.

Figure S-15

Cr-EA 1050°C, helium 75 $mLmin^{-1}$ Mass selective chromatogram of HCl (m/z 36)

Formation of hydrogen chloride as a byproduct when water is reacted at high temperature with partially chlorinated chromium. The generation of HCl reduces the yield of elemental hydrogen and may entail isotope fractionation.

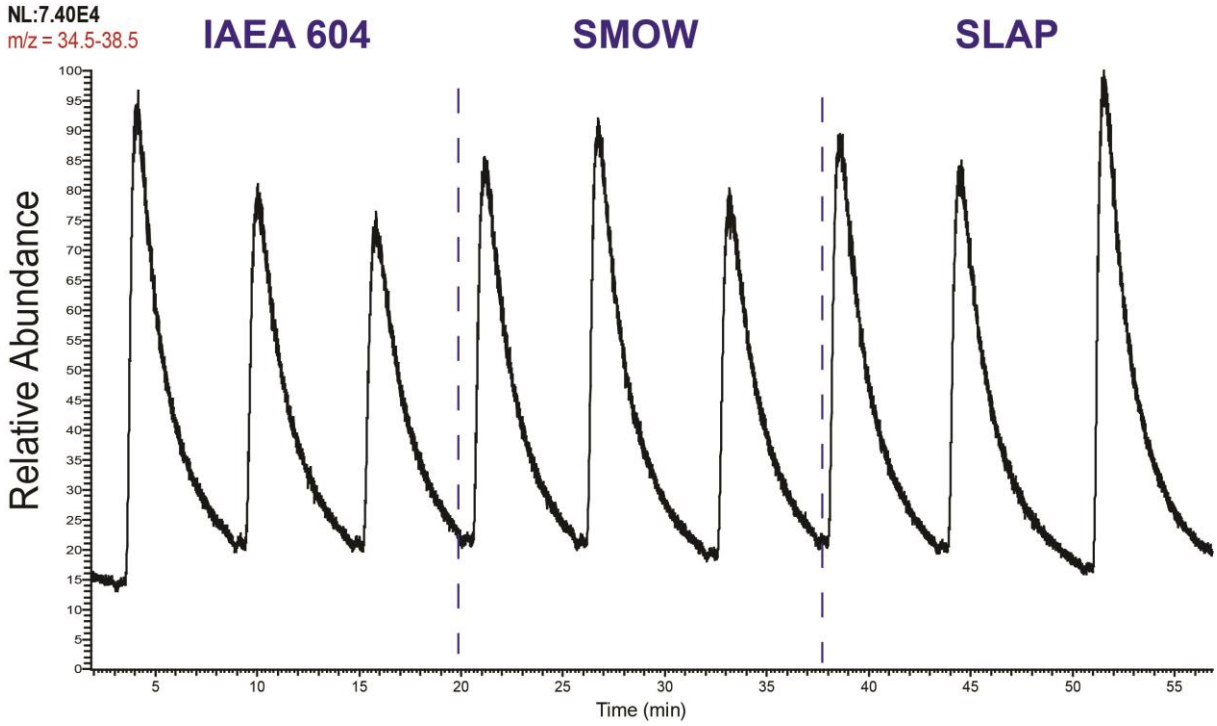


Table S-2

Hydrogen-isotope results as a result of the order of measurements (Figure 15, left to right)

Sequence of analyses	**Sample**	**Measured value / mUr**	**Accepted value / mUr**
1	IAEA-604	750	+800
2		757	
3		761	
4	VSMOW2	196	0
5		96	
6		62	
7	SLAP2	-291	-427.5
8		-342	
9		-384	

Figure S-16: Example of rector construction at the Leipzig LSI:
reactor (**A**) conventional oxidation reactor for EuroEA CHN; (**B**) newly prepared reactor filled with quartz chips and chromium powder; (**C**) chromium package after analyses of 160 samples (~ 3 mm oxidized, green color) plus metal residues from tin or silver capsules