Comparison of Isotope Analysis with Single Reactor Combustion and Conventional Combustion in a Dual Reactor Setup

Oliver Kracht,
Thermo Fisher Scientific, Bremen, Germany

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Key Words
FlashEA 1112 HT, Flash 2000 HT, EA-IRMS, BSIA Bulk Stable Isotope Analysis, N/C Isotope Analysis, Isotope Ratio MS

Introduction

The Thermo Scientific™ Flash 2000 HT elemental analyzer combines two single-furnace systems in a single analyzer, one for Dynamic Flash Combustion and one for High Temperature Conversion. When coupled to a Thermo Scientific Isotope Ratio Mass Spectrometer (IRMS), this elemental analyzer allows bulk stable isotope analyses (BSIA) of N, C, S, H and O of organic and inorganic materials as well as water and other liquids.

Upon combustion of a sample with addition of exactly timed and dosed oxygen, the sample converts to CO_2 and NO_x among other gases. Nitrous oxides are subsequently reduced to N_2. Oxidation and reduction are commonly arranged in two consecutive reactors (Flash 2000 or FlashEA 1112 elemental analyzers for IRMS).

The combination of oxidation and reduction into one single reactor for Dynamic Flash Combustion allows the implementation of a special high temperature furnace as already used in the TC/EA high temperature conversion elemental analyzer. This furnace is then used for a special ceramic reactor filled with glassy carbon to produce H_2 and CO for analysis of $^{2}H/^{1}H$ and $^{18}O/^{16}O$ isotope ratios.

The execution of combustion in a single reactor reduces the total volume of the system thus gaining in signal-to-background ratio which is particularly preferable for samples with low N content. This benefit is balanced by a lower reduction capacity: A double reactor setup allows for about 600 – 1000 samples depending on the sample type before the reduced Cu is exhausted and exchange required. The single reactor system shortens the life time of the reactor to about 150-250 samples.

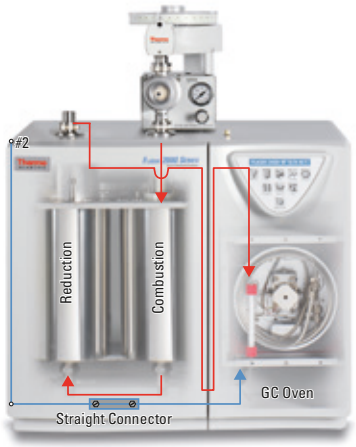

Figure 1. Thermo Scientific Flash 2000 HT elemental analyzer showing the replumbing to use with a double reactor setup for combustion.

Technique

The single reactor setup in the Flash 2000 HT elemental analyzer is given in Figure 2. It shows two dedicated reactor sections, one for combustion (Cr_2O_3) and one for reduction (reduced Cu), adjusted to the temperature profile of the furnace. The lower section is optionally filled with silvered cobaltous / cobaltic oxide to remove halogens and sulfur.

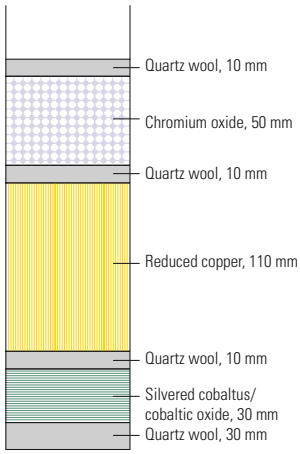

Figure 2. Reactor sections for combustion and reduction.

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For dual reactor setup, two reactor tubes, one for oxidation and one for reduction, are packed according to the instructions for N and C analysis in the Elemental Analyzer Operating Manual (PN 1158550). Besides silvered cobalt (II/III) oxide granulates (PN 33824500) the oxidation reactor is packed with Cr_2O_3 (PN 33822900) and operated at 1020 °C. The reduction reactor was filled with reduced Cu wires (PN 33835300) and inserted into the left furnace. This furnace temperature is set to 680 °C. It is recommended to use the left furnace for reduction. The heating, the regulation and the temperature profile of the high temperature furnace make this side less favorable for oxidation.

New stainless steel capillaries 1/16" are used to connect the oxidation reactor in the right furnace with the reduction reactor in the left furnace. The reduction reactor is terminated with a top connector (PN 35008421 plus nut PN 35001427). From this connector a new capillary leads to the water trap through one of the holes on top of the housing (red line in Figure 1).

The flow must also be maintained through the molecular sieve used for high temperature conversion mode if it remains in the GC oven.

The reference flow capillary from port #2 on top of the instrument is connected with the capillary leading to the molecular sieve (blue line in Figure 1) using a straight connector (PN 34714100). This allows using the exit of the high temperature conversion section (port #4) for purging of the Thermo Scientific MAS 200R autosampler.

Results

Figure 3 and Figure 4 show a dual measurement of urea with a single reactor setup and a dual reactor setup. The amount of urea in both analyses is the same, whereas the amplitude of the main mass in the single reactor setup is 2-3 times higher. The area value is identical indicating that the same amount of N_2 and CO_2 molecules were produced upon combustion. Only the signal response as compared to the background is improved in the single reactor setup. Standard analyses on both systems show expected precision with S.D. (1σ) better than 0.15‰.

Conclusion

The Flash 2000 HT elemental analyzer combined to any Thermo Scientific isotope ratio mass spectrometer allows for the dual measurement of $^{15}N/^{14}N$ and $^{13}C/^{12}C$ as well as $^{2}H/^{1}H$ and $^{18}O/^{16}O$ isotope ratios due to its hybrid character with two separate analytical units for combustion and high-temperature conversion. Modifications on the combustion side allow dedicated S isotope ratio analysis thus making the instrument a universal and compact multi-isotope analytical unit especially with the Thermo Scientific ConFlo IV universal interface.

For extended and dedicated analysis of N and C isotopes the Flash 2000 HT elemental analyzer can easily be modified into a double reactor setup with just a few steps and used as the conventional Thermo Scientific Flash 2000 IRMS elemental analyzer.

A test with more than 600 analyses of urea has shown that the reduction capacity does not cease in a dual reactor setup as compared to the single reactor so that the Flash 2000 HT elemental analyzer can also serve as a conventional combustion system with two dedicated reactors for combustion and reduction.

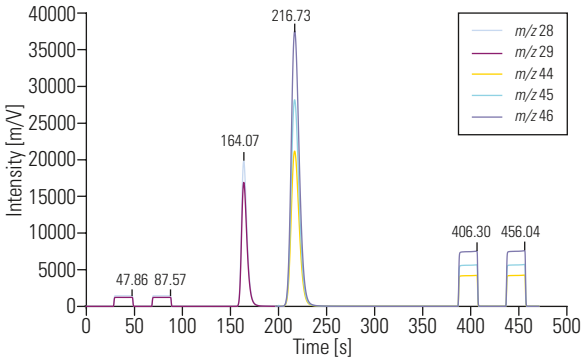

Figure 4. Resulting chromatogram of urea analysis with a single reactor setup. The amount of urea was 317 µg giving an amplitude 19810 mV and an area of 132.5 Vs (of *m/z* 28, respectively) which results in a signal response of approx. 135 mV/µg N.

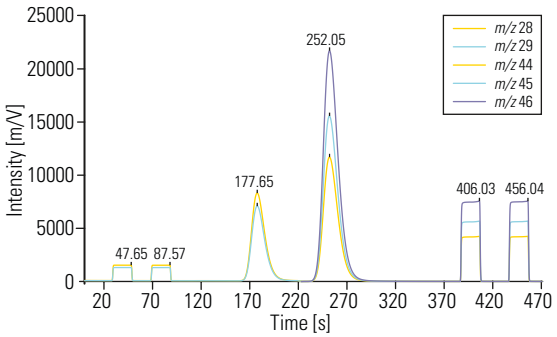

Figure 5. Resulting chromatogram of urea analysis with a double reactor setup. The amount of urea was 315 µg giving an amplitude 8246 mV and an area of 132.1 Vs (of *m/z* 28, respectively) which results in a signal response of approx. 56 mV/µg N.

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