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Read this First

This Addendum to FlashEA 1112 HT User Guide describes a few specialties to take care of when operating the instrument. Most of the pages were taken from the TC/EA Operating Manual and adapted to the FlashEA 1112 HT.

Note Carefully read through the pages. They contain important information to avoid damage to the instrument. ▲

Check for the most recent Operating Manuals and Addenda on the Customer Information Service pages (CIS) available after registration at www.thermo-bremen.com.

Introduction

High precision analysis of the stable isotopes of oxygen has been crucial for the development of stable isotope geochemistry. While procedures for the analysis of $^{18}$O/$^{16}$O of carbonates, water and silicates have been worked out early and have until recently remained largely unchanged, this is not true for the analysis of most forms of organic and inorganic oxygen.

The isotopic analysis of organic oxygen largely bases upon carbon reduction (carbon reduction method of Unterzaucher and Schütze), in which oxygen is converted to CO. The reaction is generally carried out in quartz tubes at modest temperatures (that is 400 °C-1500 °C) in the presence of graphite and nickel (as catalyst).

Since quartz contains oxygen, all current techniques are associated with a blank. Fluorine-containing samples cannot be analyzed because of the reaction of hydrogen fluoride with quartz and the subsequent water formation. A lot of samples, e.g. sulfates, cannot be measured either, because the increasing interaction of carbon and the quartz becomes unacceptable at higher reaction temperatures.

As a consequence, isotope ratio measurement of oxygen in organic matter has not kept pace with methodological advances that allowed rapid, easy and precise measurement of $^{13}$C and $^{15}$N by Dumas combustion, as embodied in the Elemental Analyzer via Continuous Flow (CF) inlet system.
To overcome these disadvantages, it was necessary to develop a new reactor design built especially for oxygen isotope analysis of a wide variety of organic and inorganic compounds (including water) at reaction temperatures up to 1450 °C. The specialty of the reactor also allows the conversion of hydrogen in sample material to H₂ gas.

The particularity of the reactor is a new two-tube technique. The so-called "High Temperature Conversion Reactor" (pyrolysis reactor) consists of an outer ceramic mantle tube made of aluminum oxide and an inner glassy carbon reactor. The space between internal and external tube is continuously flushed with helium to avoid any undesired oxidation.

**Warning** Both separation columns must be kept under helium flow (10 ml/min or higher) during measurement to avoid damage. ▲

**Note** Oxygen injection must be disabled when operating with the pyrolysis section to avoid damage of the glassy carbon tube. See arrow in Figure 1, right. ▲

![Figure 1. Disabling Oxygen Injection](image-url)
Alternative Reactor Setup for Combustion

**Note** In some cases, it can be advantageous to use copper oxide instead of chromium oxide. Reactors filled with copper oxide must be operated at 900 °C-920 °C. Check your calibration with appropriate standards to maintain analytical precision and quality after changing the reactor filling from chromium oxide to copper oxide.

**Temperature Settings**

The following procedure is recommended for increasing the reactor temperature of the combustion section when operating with chromium oxide (Cr₂O₃) at 1020 °C:

1. Increase the temperature to 900 °C. Keep it for at least 30 min.

2. Increase it to the operating temperature of 1020 °C.

3. Let it cool down in steps: 900 °C - 800 °C - 600 °C - 400 °C.

**Warning** Immediate temperature increase to 1020 °C can cause copper melting. Cooling down in steps can avoid reactor breaking.

**Maintenance Measures for Pyrolysis Section**

Due to our knowledge arising from more than 200 pyrolysis units in the field and to feedback from our users during the last ten years, we inform about maintenance measures. They may facilitate proper work, may be helpful to keep your device in good order and increase the life time of the pyrolysis reactor and the furnace heater.
Warning  As the life time of the furnace heater is limited, do not heat it to higher temperatures than necessary! ▲

This implies in detail to measure according to Table 1.

Table 1. Recommended Measurement Conditions

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxygen of organic samples</td>
<td>1325 °C-1350 °C</td>
</tr>
<tr>
<td>oxygen of inorganic samples</td>
<td>1450 °C</td>
</tr>
<tr>
<td>hydrogen of organic samples</td>
<td>1400 °C</td>
</tr>
<tr>
<td>hydrogen of inorganic samples</td>
<td>1450 °C</td>
</tr>
<tr>
<td>water</td>
<td>1400 °C</td>
</tr>
</tbody>
</table>

This implies in detail to cool down the furnace considering the following comments:

- If you do not want to perform any analysis for about one day (e.g. over night), cool down the furnace to 400 °C and set the column to 150 °C (unless GC box is used for NC analysis).

- If you do not want to perform any analysis for more than one week, cool down both furnace and column to ambient temperature.

- If the pyrolysis unit has not been in use for a long time or if it was off, heat the column to maximum temperature (that is, 190 °C) for at least 24 h. Make sure that you maintain a flow through both separation columns during baking out.

- Always watch the background of m/z 28 and m/z 40. If the values exceed those you are used to, perform a leak test. A small leak will crack the ceramic tube, and after a while the glassy carbon reactor as well.

- After 70-100 measurements (depending on size and type of samples) cool down the reactor to 500 °C. Take the graphite crucible out of the reactor using the special tool provided with the system. After cleaning, the crucible can be used again. See “Reactor Cleaning” on page 5.

- In case of a new or replaced furnace, set the heating transformer to initial voltage. See “Transformer” on page 8.
**Reactor Cleaning**

After 200-300 samples have been measured (depending on application and sample size) the reactor should be cleaned and the ash of the samples be removed. Proceed as follows.

1. Reduce the reactor temperature to 0 °C.

2. Reduce the column temperature to 0 °C.

3. Switch on He dilution, if ConFlo III is installed or close the needle valve to the IRMS.

4. After reaching the temperatures turn off the carrier gas (He). Wait for three minutes until the system is depressurized.

5. Remove the autosampler.

6. Remove the front cover plate.

7. Unscrew the bottom reactor connection.

8. Carefully pull out the reactor.

9. Carefully pour the reactor filling on a clean and dust-free surface.

10. Separate the ash from the glassy carbon granulate. The granulate is still usable, if it is shiny.

11. Exchange the graphite crucible or clean inside and outside carefully. The crucible can be reused. Refer to “Replacing Graphite Crucible” on page 6.

12. Remove deposits from inside and outside of the reactor by using the graphite rod or a bottle brush.

13. Renew the quartz wool. If necessary, renew the silver wool as well.
Replacing Graphite Crucible

After approximately 70-100 samples have been measured (depending on material and sample amount) the graphite crucible should be cleaned. See Figure 3 and proceed as follows.

1. Insert He dilution, if ConFlo III is installed or close the needle valve to the IRMS.

2. Set the reactor temperature to 500 °C.

3. After reaching a temperature of 500 °C (it takes approximately 45 min) switch off the He flow.

4. Remove the autosampler.

5. Remove the graphite tube.

6. Insert the special tool (that is, the crucible remover) inside the graphite crucible. See Figure 3.

7. Pull the graphite crucible out of the reactor using gloves.

Figure 3. Replacing Graphite Crucible
8. Drop the new graphite crucible into the reactor, or remove the deposits outside of the graphite crucible and use it again.

9. Heat up again and wait for the system to stabilize by checking the background values.

**Working with Gas Tanks**

**Warning** CO gas is toxic! When working with carbon monoxide (CO), good ventilation is essential. Otherwise, the gas can be hazardous to your health! ▲

**Warning** H₂ gas may form explosive mixtures with oxygen! ▲

**Warning** It is strongly recommended to fix the gas tanks firmly to prevent them from toppling down! ▲

1. Install an exhaust tube on top of your ConFlo II/III as shown in Figure 4 in order to remove the toxic carbon monoxide (CO) from inside the ConFlo II/III out of your working area.

**Figure 4.** Exhaust Tube for CO Removal
2. Before starting the system, perform a leak check as follows:

   a. After mounting the reducing valve to the gas tank both valves (that is "on/off-valve" and "reducing-valve") should be open.
   b. Open the main valve for two or three seconds to let the gas purge the entire valve system.
   c. Close the "on/off-valve". Then close the "main valve".
   d. Mark the manometer positions of the "on/off-valve" and the "main valve". Wait for 10-15 min. A leak may be present, if the manometer positions have changed.
   e. In order to detect a leak use soap solution on all valves and connections. Check for bubble formation. Remove the soap solution quickly and carefully after the test.

**Transformer**

Reactor heating may stop at a lower temperature than selected, because the resistor value increases over time. Therefore, a higher voltage setting becomes necessary. For a new setting proceed as follows:

1. Switch the main power supply off.

2. Remove the right side panel of the rear side.

3. Move the wire (B) to the next higher value. See Figure 5.
**Note** In case of a new or replaced furnace, set the heating transformer to initial voltage.

**Warning** Switch off main power prior to working in order to prevent an electrical shock!