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Total Digestion with HF in Multiwave GO Complexation of Fluorides

In wet chemical analysis complete dissolution of the samples is required for the determination of total contentration of elements. Especially for silicate-containing samples the usage of hydrofluoric acid is a necessity.

1 Introduction

In order to digest and extract all metals quantitatively from matrices containing silicates and oxides, normally digestion with hydrofluoric acid is carried out in a two step procedure.

The first step is the digestion with an acid mixture containing HF. The second step is the complexation of the remaining HF with boric acid. This does not only help to complex the free fluoride ions in the solution, but it also facilitates the dissolution of precipitated fluorides.
The following reactions occur during digestion:

- Digestion:

$$6\ HF + SiO_2 \rightarrow H_2SiF_6 + 2\ H_2O$$

- Complexation:

$$H_3BO_3 + 3HF \rightarrow HBF_3OH + 2\ H_2O$$

$$HBF_3OH + HF \rightarrow HBF_4 + H_2O$$

Due to safety reasons, a three-step process is recommended when using HVT50 vessels with venting technology:

- **High-temperature digestion with acids without HF**
- **Low-temperature digestion with HF**
- **Low-temperature complexation with boric acid**

2 Analytical Procedure

Step 1 - Digestion without HF

1. Weigh in the samples, add the reagent mixture (e.g. HNO_3, HCl) to the samples and blanks and close the vessels.
2. Load Rotor 12HVT50 with samples and blanks, place it into the cavity, and carry out a digestion program.

Good to know:

For more detailed information about acid mixtures, digestion and leaching programs please refer to the instruction manual Multiwave GO.

3. Open the vessels after cooling.

If the solutions contain white silicate precipitates continue with Step 2.

Step 2 - Digestion with HF

4. Add HF to the samples and blank and digest them in a run with temperature limit < 160 °C.
5. Open the vessels after cooling.

Good to know:

If there are no precipitates after the digestion, it is not always necessary to run the complexation step.

- If the HF concentration in the final solution is lower than 0.1 %, you can use the solution directly for analysis, as it will not attack glass or quartz. (Introduction systems of ICP-OES or ICP-MS are mainly made of these materials).
- If the HF concentration in the final solution is higher than 0.1 % and complexation shall be avoided, it is necessary to switch to an HF-resistant introduction system (mainly made of ceramic material).
- Another possibility to avoid the complexation step is evaporating the HF and dissolve the residue with (diluted) acids.

If solutions are mostly turbid and contain white precipitates of fluorides of K, Na, Ca, Ba, Sr, Al or Fe continue with Step 3.

Step 3 - Complexation

1. Prepare cold saturated boric acid solution adding 1 L ultra pure Milli-Q water to 60 g of solid H_3BO_3 at room temperature.
   After stirring for approx. 30 min an equilibrium between dissolved and undissolved boric acid is achieved (cold saturated solution).

2. Add 6 mL of the supernatant of this H_3BO_3 solution to the sample for each mL of used HF (40 %) for complexation.

3. Close the vessels and load the rotor.

4. Use a complexation program with temperature limit < 160 °C.

As a result, clear solutions without white precipitates are received.

Good to know:

Depending on the analytical needs, boric acid (usually available as solid, hygroscopic crystals) should be recrystallized to get a saturated solution suitable for trace analysis.

Recrystallization

1. Add 1 L ultra pure Milli-Q water to 200 g of solid H_3BO_3 and heat up the solution to approx. 70 - 80 °C to achieve a saturated solution.

2. Allow the solution to cool down slowly. Crystals with higher purity will precipitate and a supernatant - which contains the bulk of impurities - will remain.

3. Discard the supernatant. You can repeat steps 1 - 2 several times with the obtained H_3BO_3 crystals (with less and less water) to reduce the trace element blank level to a minimum.

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