Elemental Analyzer Isotope Ratio Mass Spectrometry (EA-IRMS)

Abstract

This document describes the method for determining stable isotope ratios ($^{13}C/^{12}C$ and $^{15}N/^{14}N$) by Elemental Analyzer Isotope Ratio Mass Spectrometry (EA-IRMS).

This method is applicable for natural abundance or enriched biological, sediments and suspended matter samples (Boschker and Middelburg, 2002).

This is the procedure as used in NIOO-CEME.

Keywords: fatty acids, chromatogram, NIOO-CEME .

1. Pre-processing of samples

The following types of samples can be analysed:

- Suspended particulate matter (SPM), on a Whatman GF/F filter, dried (60 ^{o}C).
- Sediment, freeze-dried and grinded.
- Biological material, freeze-dried and grinded.

To prevent contamination,

- The Ag and Sn-cups are extracted with hexane/acetone for 4 hours
- The cups are then dried at 60 ^{o}C
- They are subsequently heated to 450 ^{o}C (Ag) and 200 ^{o}C (Sn) for 1 night
- The Whatman filters are heated to 400 ^{o}C for 4 hours and stored in an exsiccator.

In order to estimate 13C/12C ratios in samples that contain carbonate, the inorganic C has to be removed with HCl. This is not necessary for 15N/14N. For sediments, this is done as follows:

- A quantity of sample corresponding to 20 to 200 μg C is put in an Ag cup.
- Add 10 μL HCl 30%, and repeat until it stops reacting (and CO_2 escapes).
- The samples are put on a heating tray heated to 50 ^{o}C, and temperature increased to 120 ^{o}C.

- After 15 minutes the samples are removed and left cooling.
- 10 μL HCl 5% is added to ensure that all inorganic carbon is removed.
- The samples are now again heated for 1 hour.
- The cups are pinched closed and (preferentially) analysed immediately, or stored at 60 ^{o}C.

For biological samples, this is slightly different:

- A quantity of sample corresponding to 20 to 200 μg C or 2-14- μg N is put in an Ag cup.
- Add 10 μL HCl 5%, and repeat with 10-20 μl HCl 5% until it stops reacting (and CO_2 escapes).
- The samples are put on a heating tray heated to 50 ^{o}C.
- After 15 minutes the samples are removed and left cooling.
- 10 μL HCl 5% is added to ensure that all inorganic carbon is removed.
- The samples are now again heated for 1 hour.
- The cups are pinched closed and (preferentially) analysed immediately, or stored at 60 ^{o}C.

For suspended particulate matter samples on a whatman GF/F filter

- The sample is weighed accurately.
- A pie is cut from the filter, corresponding to 20 to 200 μg C and put is a glass petri-dish.
- The sample is put is in exsiccator with on the bottom a petridish with HCl 37%. A slight vacuum is created, and the samples left for 20 minutes.
- After annihilating the vacuum, the samples are removed and left for a while to get rid of the HCl fumes.
- Fold the filters and put in a Sn cups.
- The cups are pinched closed and (preferentially) analysed immediately, or stored at 60 ^{o}C.

Two control samples are added as a reference: an empty Ag cup (biological and sediment sample) or a blanc GF/F filter and a sample with known composition.

2. Analysis

Oven dried or lyophilized well grinded samples are combusted at high temperature (1020 ^{o}C). Nitrous oxides are reduced with copper at 650řC to elementary nitrogen After drying the

formed CO_2 and N_2 are separated on a GC-column and carried to the IRMS in a helium flow for analyzing the ion-ratios corresponding to the isotopic composition (^{13}C and ^{15}N).

The apparatuses used at NIOO are (figure):

- the thermo Flash EA 1112 elemental analyzer, with auto sampler AS128 and Haysep-Q column 80-100 mesh I.D. 2mm
- Conflo III interface
- Isotope Ratio Mass Spectrometer Thermo Delta V Advantage

3. Calculation

After blank correction, the results are calculated with two reference material standards through normalization.

$$\delta M_{prim,r} = \frac{\delta M_{rg,m} - \delta S1_{rg,m}}{\delta S2_{rg,m} - \delta S1_{rg,m}} \cdot (\delta S2_{prim,r} - \delta S1_{prim,r}) + \delta S1_{prim,r} \quad (1)$$

where

- $\delta M_{prim,r} = \delta$ sample with respect to primary standard
- $\delta M_{rg,m} = \delta$ sample measured against reference gas
- $\delta S1_{rg,m} = \delta$ reference standard 1 measured against reference gas
- $\delta S2_{rg,m} = \delta$ reference standard 2 measured against reference gas
- $\delta S1_{prim,r} = \delta$ reference standard 1 with respect to primary standard
- $\delta S2_{prim,r} = \delta$ reference standard 2 with respect to primary standard

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