Losses Of Elements During Dry Ashing Of Biological Materials

L. Harju, J. Rajander, K-E. Saarela
Laboratory of Analytical Chemistry, Åbo Akademi University, Biskopsgatan 8, FIN-20500 Turku, Finland

J-O. Lill, S-J. Heselius
Accelerator Laboratory, Turku PET Centre, Åbo Akademi University, Porthansgatan 3, FIN-20500 Turku, Finland

A. Lindroos
Department of Geology and Mineralogy, Åbo Akademi University, Domkyrkotorget 1, FIN-20500 Turku, Finland

ABSTRACT

Particle induced X-ray emission (PIXE) and particle induced gamma-ray emission (PIGE) were used to evaluate the losses of elements during dry ashing of biological materials at different heating temperatures. The materials studied were mushrooms, marine algae and pine bark. Samples of these materials were heated in a furnace at temperatures between 105 and 1000°C. The behaviour of heavy metals like Cu, Fe, Ni and Zn were studied with PIXE. No significant volatilisation was observed for these elements at temperatures below 850°C. Losses of lighter elements like nitrogen and sodium were studied with the PIGE method. Nitrogen in pine bark was lost at 400°C. The $^{137}$Cs activity in the mushrooms was determined with an NaI(Tl) detector in a lead shield. At temperatures above 700°C the activity from $^{137}$Cs began to decrease. The total ash contents at the different temperatures are also reported. Heating of biological samples to 400-550°C is suitable for most samples prior to ion-beam analysis.

Keywords: Dry ashing, PIXE, PIGE, losses of elements, $^{137}$Cs.

1. INTRODUCTION

Dry ashing at 550°C is commonly performed for preconcentration of non-volatile elements in biological substances prior to the analytical determination. Dry ashing is used for the removal of the organic matrix in biological samples [1]. The obtained increase of the concentrations for many trace elements of interest is useful e.g. in ion-beam analyses [2, 3]. The ashed samples are then analysed and the concentrations in the biological samples are calculated considering the ash content. It has earlier been shown that the gain in sensitivity in ion-beam studies depends on the ash content as most ashes of biological materials have similar matrix compositions [2, 3]. In a few cases the ash residue contains a lot of sodium, which will have a negative effect on the detection limits in ion-beam analyses [4]. There is unfortunately also a possibility that some elements of interest escape during the dry-ashing process [5]. To investigate these elemental losses several materials were heated at different temperatures and the residues were analysed with particle induced X-ray emission (PIXE) and particle induced gamma-ray emission (PIGE) methods.

2. EXPERIMENTAL

2.1 Dry ashing

Pine bark (Pinus sylvestris), mushrooms (Cantharellus cibarius) and marine algae were dried in an oven at 105°C in order to obtain the concentration on dry matter basis. The marine algae was a commercial
product of edible dried Japanese algae (Noria) and the mushrooms were picked in 1996 in southwestern Finland (x=22°35’43’’E, y=60°39’58’’N). The dried materials (10-50 g) were weighed into porcelain crucibles and heated in a Vulcan 3-130 programmable furnace. The heating process was performed by slowly increasing the temperature (25°C/h) to 250°C and then keeping the temperature for 6 hours. The procedure was repeated for 400, 550, 700, 850 and 1000°C (Fig. 1). After each heating step an aliquot (100-200 mg) was removed for ion-beam analyses. The materials were almost completely ashed at 550°C and only a small decrease in mass is observed at the higher temperatures.

**FIGURE 1.** Mass reduction for some biological samples at different temperatures.

**FIGURE 2.** Activity of $^{137}$Cs in a sample of mushrooms (Cantharellus cibarius) from southwestern Finland calculated on dry matter basis.

### 2.2 Instrumental methods

The heated materials were pressed to pellets. These were irradiated with ions from the Åbo Akademi University MGC-20 cyclotron for PIXE and PIGE analyses. In the PIXE analyses the pellets were irradiated in air with a beam of 3 MeV protons incident on the target [2]. An intrinsic germanium planar detector was used to measure the X-rays emitted. The integrated charge needed for quantification was determined from measuring light emission induced in air by the particle beam. The GUPIX software [6] was used for quantification of the peak areas in the obtained X-ray spectra.

PIGE was employed for the analyses of the lighter elements [3]. The proton beam energy was raised to 4.2 MeV incident on the target and the samples were irradiated in a helium atmosphere to avoid interference from nitrogen in air. A 4 µm thick nickel foil used as beam exit window emitted suitable gammas for charge normalisation. The contribution from the nickel in the samples was insignificant. Biological certified reference materials were used for the evaluation of the PIXE and PIGE results [2, 3].

The mushrooms in southwestern Finland contain $^{137}$Cs from the nuclear accident in Chernobyl. The activity in the ashed mushroom samples was measured in the autumn of 2003 with an NaI(Tl) detector within a lead shield for three hours each. The activity is rather constant up to 700°C but drops at higher temperatures (Fig. 2). Koh et al. [5] noted that caesium in pepperbush decreased already at 500°C and above. The stable caesium is expected to have a similar chemical behaviour as $^{137}$Cs. The $^{137}$Cs/Cs ratio for mushrooms from Kullaa, Finland have been determined to about 5000 Bq/mg [7] and the content of stable caesium in our mushroom sample is therefore estimated to 1 µg/g of dry weight. The detection limit for caesium using dry ashing at 550°C for preconcentration and PIXE is then 5 µg/g.
3. RESULTS AND DISCUSSION

3.1 Losses of elements

The mass reduction during dry ashing is due to the removal of carbon, hydrogen, nitrogen and partly oxygen. Oxygen forms oxides and carbonates with the remaining ions. PIGE analyses show that about 90% of all carbon and nitrogen are removed at 400°C. The concentrations of both elements are below the limits of detection (LOD:s) at 550°C. There is also a loss of chlorine and bromine at these temperatures. In the marine algae a reduction of chlorine by a factor of 10 was observed at 250°C and sulphur and bromine were reduced to a quarter at 550°C (Fig. 3). The concentrations for the biological materials are given on dry matter basis. There was no significant change in the concentration of phosphorous in marine algae. Most of the other elements are quite stable up to 700°C. In pine bark most of the chlorine and nitrogen were lost already at low temperatures (Fig. 4). At 850°C these elements were completely lost. Sodium in pine bark showed a decreasing trend and could not be found in the residue when heated at 1000°C. The concentrations of Ca, Cu, Fe, Mn, Ni, Sr and Zn did not decrease during the heating.

![FIGURE 3. Loss of elements in marine algae at different temperatures.](image1)

![FIGURE 4. Loss of elements in pine bark at different temperatures.](image2)

Potassium and rubidium were well preserved in marine algae and mushroom samples at all temperatures but showed a decreasing trend in pine bark. Koh et al. [5] recommended heating temperatures below 450°C to avoid losses of alkali metal elements. According to our results, heating to 400°C is sufficient for most biological materials prior to ion beam analysis methods.

REFERENCES


Proceedings of the 10th International Conference on Particle Induced X-ray Emission and its Analytical Applications, Portorož, Slovenia, June 4-8, 2004