

**LOSSES OF RADIONUCLIDES RELATED TO
HIGH TEMPERATURE ASHING**

**Göran Carlsson
Swedish State Power Board
Ringhalsverket**

**S-430 22 VÄRÖBACKA
SWEDEN**

ABSTRACT

When measuring radionuclides in samples from the environment of nuclear power plants, a sample preparation step, such as high temperature ashing is often necessary.

Although much used, this method is subject to controversy because of the risk of losses of several elements. A study, including the ashing of synthetically prepared samples was undertaken. Controlled and moderate temperature rise rate and a final temperature not exceeding 550 C was shown vital for recovery.

INTRODUCTION

To reach reasonably low limits of detection and to achieve good representativity when measuring radionuclides in the environment, large samples, usually at least 1 kg, are often necessary. Direct counting of such a large amount of material may be impractical and unefficient. The radionuclides of interest must therefore be segregated from the rest of the sample. In biological samples this usually means removal of water and/or organic matter.

Among the drying techniques used, hot air drying and freeze drying can be mentioned. Most radionuclides of interest in environmental samples will not be seriously affected by this step, (some, like H-3 in the form of tritiated water will, however, be affected, and should therefore be subject to special consideration and methodology).

To remove organic matter the drying step is usually followed by wet or dry combustion (ashing). Wet combustion has the advantage of being performed at a relatively low temperature (100 C), which reduces the risk of volatilization. Wet combustion of these large amounts of material will however be expensive and, in normal laboratories, impractical.

Dry combustion, on the other hand, is easily performed and inexpensive, but has the disadvantage of using temperatures as high as 600-700 C. At these high temperatures there is always the hazard of losses, due to volatilization. Control of several parameters can be shown to be of importance when trying to minimize losses. Of special importance is the rate of temperature elevation, the final temperature and the matrix composition.

Fast temperature rise has been shown to cause losses of several elements (1). Temperatures exceeding 550 C are usually not recommended (1,2). Matrix chlorides, especially in the form of ammonium-chloride, are suspected to cause high losses of many elements (1). The formation of volatile organometallic compounds has, in other instances been proposed to cause low recovery (1). Phosphate, on the other hand, has been reported to prevent the loss of cesium (1).

This complex situation, with several mechanisms competing, makes it obvious that every laboratory, introducing a dry-ashing method, has to do all the checks necessary to confirm that their methods, equipment and samples will work well together.

METHODOLOGY

The National Swedish Environment Protection Board is the authority responsible for the methods used in preparation of samples collected in the environment of the Ringhals nuclear power plant. The methods prescribed are, however, not detailed enough to cover every single aspect that might be of importance for recovery. This, and

the fact that several authors stress that apparently minor changes in ashing techniques might lead to dramatic changes in recovery made it clear that we had to undertake a study of our own. The basis of this study should be to verify that methods, so far used, had not resulted in unacceptably high losses. In subsequent steps we wanted to acquire more information on the influence of certain parameters, suspected to reduce recovery.

To minimize the self-absorption and coincidence effects that might complicate the evaluation of the results, we decided to use a point-source geometry at a fairly long distance from the detector. This in combination with the demand for not too long counting times called for a sample activity many times higher than normally present in environmental samples. A synthetic sample had to be prepared.

To get a realistic mix of radionuclides about 200 g of strong cation and anion ion exchanger in the form of powder was suspended in 10 l of reactor coolant from the BWR at Ringhals. The ion exchanger was filtered off and left to dry and decay in a desiccator for about 2.5 months. When the shortlived nuclides had decayed, the mix was expected to contain all non-natural nuclides usually found in the environment in realistic proportions. However, because of its low concentration in the reactor coolant, Cs-137 was later added, bound to a cation ion exchanger.

From this resin an aliquot of 3-4 g was taken and counted in a small plastic vial at a distance of 40 cm. The resin was thoroughly mixed with 20 g of sand (or, in one case, commercial, dried dog food). The mix was then ashed, using one of several methods to be tested. The residues were transferred to the same type of plastic vial as before and counted once more with the same geometry and detector. The transfer of the residues from the porcelain crucible to the counting vial was fairly difficult due to static electricity. It was necessary to wipe off the inner walls of the crucible with a small piece of moist filtering paper.

The furnace used was a Leybold-Heraeus muffle furnace, capable of a final temperature of 1300 C. The furnace was combined with a JUMO programmable temperature controller. Temperature calibration of the furnace was done using a thermo-couple device.

The gamma-spectrometric counting was done with two high purity germanium detectors with a sensitivity of 17% resp. 20% (compared to a 3"x3" NaI crystal). Spectra were collected and evaluated in a ND 8700 system using standard ND software.

RESULTS

Results are listed in table 1. Displayed uncertainty figures are the total uncertainty as calculated from triple samples. Sb-124 is not excluded, in spite of its low counting precision, because it is known to be volatile.

Table 1: Recovery

	METH.1	METH.2	METH.3	METH.4
Cr-51	99+/-6	91+/-2	101+/-2	90+/-2
Mn-54	102+/-2	91+/-2	101+/-7	101+/-4
Co-58+				
Co-60	98+/-5	90+/-1	99+/-4	97+/-2
Zn-65	95+/-12	97+/-6	100+/-3	99+/-5
Ag-110m	105+/-5	91+/-7	90+/-10	84+/-8
Cs-137	96+/-5	92+/-3	77+/-6	90+/-1
Sb-124	92+/-20	98+/-18	89+/-6	103+/-22

Meth.1: 175 C for 2h + 350 C for 2h + 450 C for 2h + 550 C for 18 h.

Meth.2: Like meth.1 but 3 ml of 3M KCl was added to the sample before ashing

Meth.3: Like meth.1 but the final temperature was 650 C.

Meth.4: The saw-dust matrix was exchanged for commercial dogs food. The sample was placed in a cool furnace and the temperature was elevated to the final temperature as fast as possible, which means in about 1 hour. The ashing time at final temperature was 23 hours. Final temperature was 550 C.

DISCUSSION

Among the elements listed in table 1 all except Mn and Co have been proposed to be volatile at normal ashing temperatures. With meth. 1, which is the standard method so far used at Ringhals, losses seem to be less than 5% (1, 2).

Adding KCl was expected to increase the losses of many elements. The observed effect was, however, minimal and in no case larger than 10%. One author has observed that a matrix of sodium chloride did not cause any losses but a matrix of ammonium chloride did. This fact and the fact that a matrix of organic matter does contain a lot of amino groups in combination with chlorides makes it obvious that a further investigation is of great value here. The rising of the final temperature to 650 C had an obvious effect on the losses of Cs, Sb and (probably) Ag. This pattern was very much the same as the one published by Saiki (2).

In the last method both the matrix and the ashing procedure were changed. A controlled and moderate temperature rising rate has been proposed to be of major importance with respect to recovery. The losses observed were fairly small.

CONCLUSIONS

A standard procedure of ashing, with a moderate temperature rise rate and a final temperature not exceeding 550 C seems to be adequate for the preparation of environmental samples. The influence of chlorides on recovery should be further investigated.

REFERENCES

1. IAEA Technical report No. 118, page 33-36, Vienna 1970.
2. M. Saiki et al, *ibid*, page 81-92.