Radioanalytical Methods: Data Quality, Method Validation and Use of Standard Reference Materials

VALIDATION OF METHODS FOR THE DETERMINATION OF ALUMINIUM IN FISH GILLS BY INAA AND ICP-MS

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In a European study of fish death in mixing zones of rivers with different acidities a reliable determination of Al and other elements in gills from freshwater fish was required, and both INAA and ICP-MS were studied as candidate reference methods. INAA requires minimum sample handling with a correspondingly small risk of contamination and no blank value; however, a careful study was needed of both nuclear interference from P and the increased detection limit caused by other major elements in the sample, before reliable results for Al could be ascertained. ICP-MS requires dissolution of the sample with a resulting risk of contamination and a significant reagent blank; while sensitivity was good, the interference from N created problems for sample decomposition in the microwave oven. Our experience with actual samples indicates that both methods suffer from considerable contamination problems, requiring that samples be handled in a clean bench with superpure reagents. Nuclear interference was determined experimentally by irradiating stoichiometric P-compounds with and without a Cd-shield; the observed interference of 1 µg Al from 50 mg of P was found to require no correction in almost all cases. The accuracy of results was ascertained by analyzing SRM 1577 Bovine Liver.

Concentrations of several trace elements in lakes and rivers in the Scandinavian countries have been found to increase as a result of acid precipitation associated with the combustion of fossil fuels. Higher levels of aluminium in particular may be causing fish death in mixing zones of rivers with different acidity1, and this has initiated a European Community project under the STEP programme to study this effect.

It was decided to carry out trace multielement analysis of fresh water and fish by inductively coupled plasma mass spectrometry (ICP-MS), permitting direct determination of up to 49 elements2 including Al.

As a quality control, a fraction of the fish samples were also analyzed by instrumental neutron activation analysis (INAA). Verification of results by ICP-MS is therefore based on the validation of the INAA method, which was carried out with special reference to the determination of aluminium in fish gills.

Neutron activation analysis

In accordance with the BIPM philosophy3 validation of an analytical method requires that results are in a state of statistical control and have been corrected for all systematic errors.
Statistical control is ascertained by subjecting results $y_i$ and their associated standard deviation $\sigma_i$ from replicate analysis to the Analysis of Precision by calculating the statistic

$$T = \sum_{i=1}^{n} \frac{(y_i - \bar{y})^2}{\sigma_i^2}$$

where $\bar{y}$ is the weighted mean of $n$ results.

The statistic $T$ is closely approximated by a $\chi^2$-distribution with $n-1$ degrees of freedom, when results are in statistical control.

Data processing: Computer programs for the processing of counting data are validated by calculating results from replicate countings of the same sample. In this case we irradiated three different BCR environmental reference materials for 10 s in the pneumatic tube facility of the DR 3 nuclear reactor at a neutron flux density of $2 \times 10^{13}$ n/cm$^2$s.

Each sample was counted for 3 periods, first for 2 min, then 5 min, and finally 10 min, without changing counting position. The results obtained from all identifiable photo peaks were used in calculating the statistic $T$ in accordance with eq. (1). Values of $T$ for 9 different elements in 3 different reference materials were obtained from replicate determinations of 21 different photpeaks and presented in Table 1. With a total $T = 399$ for 53 degrees of freedom statistical control is clearly not maintained.

A statistical control chart is shown as Fig. 1 with $P(\chi^2 \leq T)$ in % for each peak observed in the spectra from BCR 061 Aquatic plant. All peaks are well within the 95 % control limit.