

Analytical note

# Comparison between X-ray fluorescence and inductively coupled plasma atomic emission spectrometry in the analysis of sediment samples

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## Abstract

Two multielemental analytical techniques, X-ray fluorescence analysis (XRF) and inductively coupled plasma atomic emission spectrometry (ICP-AES) were used for the analysis of the elemental composition of sediment samples from a marsh and standard reference materials. The sediment samples were pretreated with different methods which are widely used in practice. A comparison was made not only between the concentrations obtained by the different methods, but also between the statistical conclusions derived from the processing of the experimental results. Good agreement was found for some elements, e.g. Mn, Zn and Sr, while the concentrations and the statistical conclusions were shown to depend on the analytical method used in the case of other elements, e.g. Fe and Zr. © 1997 Elsevier Science B.V.

**Keywords:** Inductively coupled plasma emission spectrometry; Sample preparation; X-ray fluorescence

## 1. Introduction

Both techniques of energy-dispersive X-ray fluorescence analysis (XRF) and inductively coupled plasma atomic emission spectrometry (ICP-AES) are widely used for multielemental analysis of environmental samples [1–4]. It is sometimes difficult and time consuming to undertake a total elemental analysis following the ICP-AES method because the sample must usually be dissolved [5,6]. It is well known that sometimes it is difficult to dissolve sediments and soils, as some parts may be filtered out during the sample preparation procedure. The direct analysis of solid samples with electrothermal vaporization (ETV) is not widely applied in routine analysis. Clearly, in the sample treatment, loss

of some elements or sample contamination may occur [1]. X-ray fluorescence analysis is a non-destructive method, possessing the advantage that the total elemental content of the samples can be obtained without any complicated sample pretreatment.

The aim of the present study was to compare the two analytical methods in sediment analysis. We investigated the effects of sample pretreatments and the analytical method used on the statistical comparison of the different sediments. Systematic errors occurring during sample pretreatment and analysis were also considered.

## 2. Experimental

In order to investigate the problem presented above, sediment samples were collected from four different

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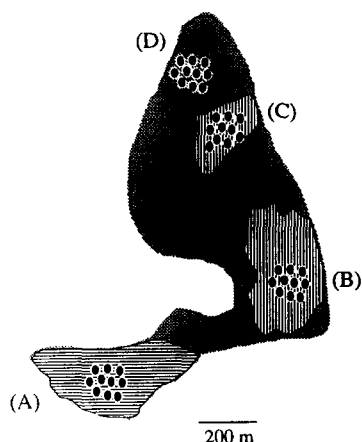


Fig. 1. Sampling sites on a freshwater marsh, Nagy-Mohos, north-east Hungary. (A) Phragmites stand; (B) *Salix cinerea* stand; (C) clear-cut area; (D) Typha stand.

patches of a natural protected marsh in northeast Hungary. Ten soil samples were collected from the upper 10 cm layer of each sampling site characterized by different vegetation (see Fig. 1). The specimens were dried at 105°C and were homogenized in an agate mortar before further processing. Each of the 40 sediments was divided into three subsamples and three different sample pretreatments were applied, respectively.

In the digestion step in the teflon bomb, 600 mg of dried matter was digested for 3 h with 5 cm<sup>3</sup> of 65% (m/m) HNO<sub>3</sub>, at 120°C. The solutions were filtered and diluted with distilled water to 25 cm<sup>3</sup> volume. This pretreatment was applied to the ICP-AES technique only. The standard reference materials (SRM) were also digested using this method for the ICP-AES measurements.

Ashing was carried out at 500 and 900°C for 5 h. For ICP-AES measurements, 500 mg of the ashed material were dissolved in 10 cm<sup>3</sup> 65% (m/m) HNO<sub>3</sub> at 80°C. After filtration, the solutions were diluted with distilled water to 25 cm<sup>3</sup> volume. One pellet of 10 mm diameter and 200–300 mg cm<sup>-2</sup> weight was pressed from each sample for the XRF analysis. The same sample preparation steps were used for SRM-s without ashing for the XRF measurements. Three to five pellets were pressed from each standard material.

A spectroflame instrument (made by SPECTRO GmbH, Cleve, Germany) was used for the ICP-AES

measurements in simultaneous multielement and sequential operation mode. Excitation was performed with a 27.12 MHz RF generator at 1.05 kW energy and nebulization with a Meinhard nebulizer using Ar at 0.6 l min<sup>-1</sup> as the nebulizing gas, 14 l min<sup>-1</sup> as the cooling gas and 0.8 l min<sup>-1</sup> as the plasma gas. Line and background intensities were both integrated for 10 s.

The XRF measurements were carried out using a Si(Li) spectrometer of 190 eV FWHM at the Mn-K $\alpha$  line. The characteristic X-ray lines were excited by an annular <sup>125</sup>I radioisotope source. The AXIL software package was used for spectral deconvolution and for the calculation of the concentration [7]. The quantification was completed by the elemental sensitivity method.

The precision of the analytical techniques was estimated by measuring three to five replicates. The error of reproducibility was less than 5% for both analytical methods, regardless of the measured element.

Concentrations of Fe, Mn, Sr, Zr and Zn were compared using two-way analysis of variance [8] separately for the different analytical methods. The two factors chosen were the type of sediment (Sed1, reed peat; Sed2, willow peat; Sed3, willow peat from a clear cut area; Sed4, cuttail peat) and the sample pretreatment (TEF, digestion in teflon bomb; 500°C, ashing at 500°C; 900°C, ashing at 900°C). The interaction between the types of sediment and the pretreatments was also considered. Multiple comparison test for all possible differences among the means, corrected for the fact that the comparisons are not statistically independent, was carried out by the least significant difference method [8]. The difference between the concentrations determined by the different analytical methods were investigated by means of a correlation analysis and by a two-sample *t*-test [8].

### 3. Results and discussion

The ashing procedures at different temperatures were compared by plotting concentrations measured after ashing at 900°C vs. those determined after ashing at 500°C. In order to investigate the correlation between the two analytical methods the concentrations determined by ICP-AES were plotted against

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