LECTURE

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An Energy-dispersive Miniprobe Multielement Analyzer (EMMA) for direct analysis of Pb and other trace elements in peats

Abstract An Energy-dispersive Miniprobe Multielement Analyzer (EMMA) was designed and constructed for sensitive, rapid, and non-destructive analysis of trace elements (As, Cr, Cu, Fe, Ga, Ge, Hf, Mn, Ni, Pb, Rb, Se, Sr, Th, Y, U, Zn) in small (e.g. 50 μm) samples such as individual mineral grains from rocks. An alternative configuration of the EMMA instrument is described here for use with larger samples such as powders of coal, soil, sediments, and plant materials. To minimize heterogeneity problems, a larger X-ray beam size (0.1×6 mm) was used by installing a different collimator, and the sample holder rotated 25 times per minute. Using this approach, Rb, Sr, Cu, Zn and Pb were measured in peat samples collected from bogs in Switzerland and northern Scotland. The detection limit for Pb, for example, is approximately 0.3 μg/g which is one order of magnitude better than conventional XRF analyzers. For comparison, Pb was also measured in acid digests of the same samples using GFAAS. The Pb results obtained using EMMA are comparable to the GFAAS data for the continental peat samples. However, in the Cl-rich samples from the maritime bogs, the GFAAS signal was strongly suppressed, and an accurate comparison of the two methods was not possible. The EMMA technique, therefore, has three advantages over conventional GFAAS: first, no sample dissolution is required; second, several elements of interest are determined simultaneously; and third, the EMMA technique is not subject to matrix interferences.

Introduction

The conventional approach to trace element analyses of environmental samples has usually been to dissolve the sample and to measure trace elements either using a spectroscopic technique such as AAS for single element analyses or ICP-AES for the measurement of a variety of elements simultaneously. More recently, the marriage of ICP spectroscopy and mass spectrometry (ICP-MS) has combined the advantages of multielement spectroscopic analyses with the great sensitivity of mass spectrometry. The greatest single advantage of all these techniques is the excellent sensitivity for most of the elements of interest, especially using graphite furnace AAS and ICP-MS. Like all analytical methods, however, these techniques are not without their drawbacks. The main disadvantage is that solid samples must be dissolved before they can be analyzed. The ramifications of sample dissolution are a), it is time-consuming, even with state-of-the-art microwave dissolution systems, b) it can be expensive, especially if high purity acids are used to minimize blank values, and c) it is destructive. For some environmental applications, sample destruction is simply unacceptable.

There are some analytical techniques which avoid sample destruction. For example, X-ray fluorescence techniques have been used for many years for analyzing both major elements (Si, Ti, Al, Fe, Mg, Ca, Na, K, P, S, Cl) and trace elements (Cr, Mn, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Pb, Th) in such samples as rocks, soils, plants and other biological materials [1]. While the detection limits for heavy metals such as Pb are much higher than with GFAAS and ICP-MS, there is no need to dissolve the samples. Commercial XRF instruments, however, require relatively large samples e.g. 200 mg or more of a powdered solid; this can be a serious limitation for many kinds of environmental studies. For analyzing small samples (e.g. single mineral grains from rocks, soils, sediments, etc.), electron microprobe analyzers (EMPA) have been used extensively and are also widely available. Unfortunately, the lower limits of detection (50 to 200 μg/g for many elements) are generally inadequate for the determination of trace elements in most environmental samples [2, 3]. Clearly then, there exists a need for a non-destructive method of measuring trace elements is very small samples.

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More than 10 years ago, the first Energy-dispersive Miniprobe Multielement Analyzer (EMMA) was designed and built in Kiev. The main goal at that time was to have an X-ray fluorescence instrument capable of rapidly analyzing a variety of trace elements in small, individual mineral grains such as apatite, garnet, monazite, sphene, zircons, and other accessory minerals from igneous rocks [4]. Having developed the instrumentation, software, and the necessary technical expertise, EMMA has more recently been applied to environmental analytical problems. For example, Pu and U were measured in "hot particles" released from the nuclear reactor accident at Chernobyl [5]. Individual samples of these particles, ranging in size from 10 to 50 μm, were analyzed directly using this nondestructive technique.

The purpose of the present paper, however, is to show how a larger excitation beam and a rotating sample holder allow the EMMA instrument to analyze bulk samples such as powdered biological materials. Of particular importance was the application of the EMMA instrument to measure Pb and other trace elements in peat samples from bogs. "Ombrotrophic" bogs are peatlands in which the surface layers are raised beyond the influence of groundwaters, and receive their inputs only from atmospheric deposition [6]. By studying the metal concentration profiles and age-dating the samples, the historical record of atmospheric metal deposition (past several thousand years) may be determined [7].

Instrument design and operation

Instrument design. The EMMA instrument is a small desk-top XRF system consisting of a conventional X-ray tube with Mo anode, focused LiF (220) variable wavelength monochromator, and sample holder [4]. Detection is accomplished with a 28 sq. mm Si(Li) detector. The spectrometer consists of a pulse amplifier, 12 bit Wilkinson analog to digital converter, interface card, and IBM-compatible computer.

The excitation X-ray beam is focused from a concave (Johansson) LiF monochromator. In the miniprobe mode, an X-ray beam 0.1 × 0.5 mm is used. The instrument has been used in this mode to measure trace elements in bulk samples such as powders of soils [8] and coals [9]; this was accomplished by analyzing 3 spots per sample and averaging the measured concentrations. One obvious problem with the miniprobe approach for analyzing such large samples is the natural variation in measured metal concentrations due to sample heterogeneity. To circumvent this problem and improve precision, the beam size was increased to 0.1 × 6.0 mm using a different collimator, and a rotating sample holder built to allow sample 25 rotations per minute. With a 1000 s analysis time, the samples are thus rotated more than 400 times per analysis. The results presented here were obtained using this configuration.

The X-ray tube is usually operated at a voltage of 50 kV and a current of 15 mA. Because monochromatic X-ray radiation is used for excitation (17.44 keV), a low background is achieved and detection limits are better than with conventional XRF instruments. For example, the detection limits for trace elements in coals with this configuration (Mo K$_\alpha$) is given in Table 1.

Calibration and limit of detection. A representative X-ray spectrum of trace elements in a peat sample is shown in Fig. 1. The instrument was calibrated for Pb using the following certified standard reference plant materials (with Pb concentrations in μg/g): NIST SRM 1547 Peach Leaves (0.87); NIST SRM 1575 Pine

Table 1 Estimated detection limits for trace metals in coals and plants. Measurements were made using EMMA in the miniprobe mode with a 200 s analysis time. Three spots were analyzed per sample, and the results averaged. Samples consisted of a variety of international certified standard reference materials from the USA (NIST), the European Community, and South Africa

| Atomic No.	Element	Detection limit (μg/g)	Relative standard error[a] (%)	
24	Cr	12	15	K Series
25	Mn	8	10	
26	Fe	7	7	
28	Ni	3	15	
29	Cu	2	5	
30	Zn	1.4	8	
31	Ga	1.3	10	
32	Ge	1.2	15	
33	As	0.8	7	
34	Se	0.5	5	
35	Br	0.5	5	
37	Rb	0.6	5	
38	Sr	1.0	5	
39	Y	1.3	10	
79	Au	2.5	10	L Series
80	Hg	1.2	10	
81	Tl	0.9	10	
82	Pb	0.6	10	
83	Bi	0.7	10	
90	Th	3.5	10	

[a] The relative standard error depends on the concentration of the element in the sample. The values given here apply to measurements at concentrations 30 times the limit of detection
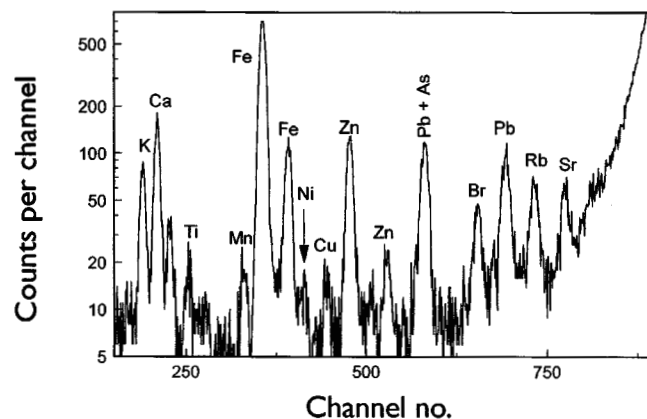
Fig. 1 X-ray fluorescence spectrum of a typical peat sample from an ombrotrophic bog in Switzerland

Needles (10.8); BCR 62 Olive Leaves (25.0); BCR 60 Aquatic Plant (63.8). A typical calibration curve for Pb is shown in Fig. 2. Using a 1200 s measuring time, the calculated minimum detection limit for Pb is 0.33 μg/g. Compared to conventional XRF methods for Pb measurements in soils and sediments [10], the detection limit for Pb with EMMA is about one order of magnitude lower.

Sample collection and preparation. Complete peat cores were collected from two bogs in the Jura Mountains of Switzerland: Etang de la Gruyère (EGr) consists of more than 6 m of peat representing more than 10,000 years of peat formation while at La Tourbière des
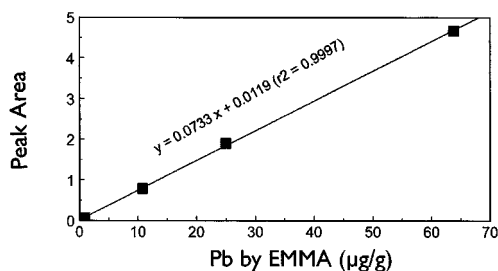
Fig. 2 Calibration curve for Pb in plant certified reference materials. The standards contained 0.87, 10.8, 25.0, and 63.8 µg/g Pb (see text)

Genevez (TGe) approximately 1.5 m of peat has accumulated over the past 5,000 years [11]. The peat samples were dried at 105°C in acid-washed Teflon bowls, and macerated in a centrifugal mill equipped with a Ti rotor and 0.25 mm Ti sieve (Ultracentrifugal Mill ZM 1-T, F. K. Retsch GmbH and Co., Haan, Germany). Lead concentrations were measured in solid peat samples using the EMMA as described here with no further sample preparation.

In addition, Pb was measured in acid digests of the same samples using GFAAS. Digestions were carried out in Teflon bombs in an MLS 1200 microwave digestion system (Milestone S.R.L., Sorisole, Italy). The peats (250 mg) were digested in 4 ml HNO_3, 3 ml H_2O_2, and 1 ml HF (all Merck Suprapur quality). Lead concentrations in the samples were measured on a Varian SpectAA 300/400 spectrophotometer using the method of standard additions.

Results

Pb in peat samples from continental bogs (Switzerland)

The Pb concentrations measured using EMMA and GFAAS in two peat cores are shown in Fig. 3. The agreement between the two methods is generally good, with the GFAAS data on average only 11% lower than the XRF values. In a recent comparison of Cu, Ni and Zn analyses of soils by XRF and ICP [12], the concentrations determined using ICP were also slightly lower, probably because of an incomplete dissolution of the samples. The completeness of dissolution of the peat samples has not yet been investigated, so this may partly explain the differences between the EMMA and GFAAS results. Perhaps more important, however, the recovery tests of Pb in acid digests of certified standard reference materials were poor, especially at low Pb concentrations, possibly because of the complex matrix.

Pb in peat samples from maritime bogs (Scotland)

Peat samples were also collected from bogs in northern Scotland and the Shetland Islands. However, reliable measurements of Pb were problematic in some of these samples using the EMMA instrument, and in all of the samples analyzed using GFAAS. At the Loch Laxford bog (LL) in northern Scotland, for example, in peat samples from depths greater than approximately 70 cm, Pb concentrations were at or below the detection limit with
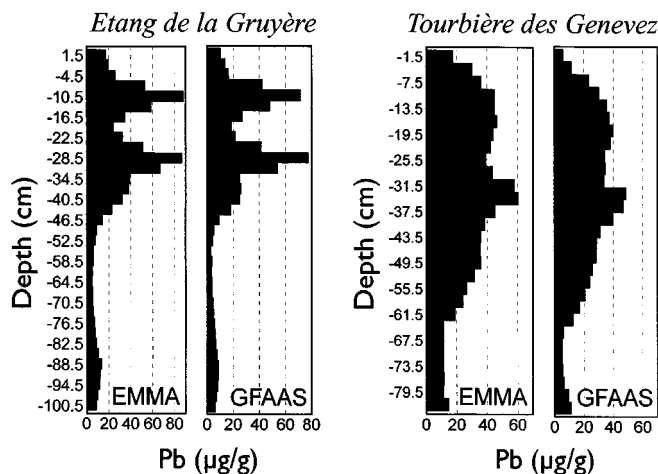
Fig. 3 Pb concentrations in two peat profiles in the Jura Mountains of Switzerland. Pb values were obtained using XRF analyses of solid samples, and GFAAS measurements of acid digests of the same samples
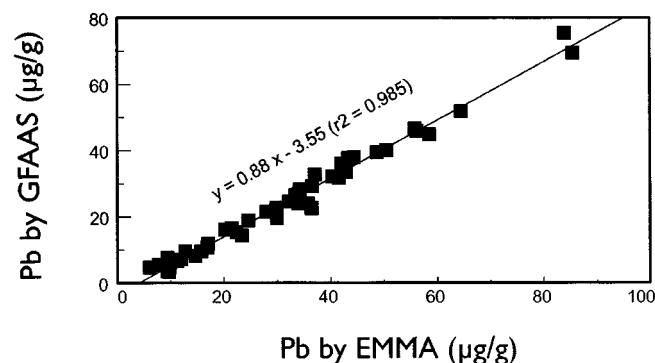
Fig. 4 Scatter diagram of Pb obtained using GFAAS versus Pb from EMMA. The GFAAS data are consistently lower, either due to incomplete dissolution or because of the complex matrix

EMMA (0.3 µg/g). This was also true for peat samples deeper than 150 cm at EGr, and corresponding to ages approximately 3000 years b.p. and older. To measure Pb in these samples, therefore, a more sensitive analytical method is needed.

With respect to the GFAAS measurements of Pb in the samples from Scotland, the absorbance signal was strongly reduced relative to the samples from Switzerland. For a given Pb concentration, the GFAAS absorbance values in the Scottish digests were approximately 3 times lower than in the digests of the samples from Switzerland. The difference in instrument response may have been due to the higher Cl concentrations in the maritime peat samples which typically contain 4 to 5 times more Cl than the peats from Switzerland. Lead complexation by Cl^- in these samples may have lowered the atomizing temperature, thereby leading to losses of Pb by volatilization. Additional work is also needed, therefore, to measure Pb in the Cl-rich peat samples from Scotland.

Comparison with other methods for analyzing solid samples

The peat profiles shown here have also been analyzed using instrumental neutron activation analysis (INAA). While Rb and Sr can be measured using INAA, the detection limits (1 and 10 μg/g, respectively) were found to be inadequate for the most of the peat samples. In contrast, the detection limits for these two trace metals using EMMA (0.5 and 1 μg/g, respectively) allowed Rb and Sr to be quantified in all of the peat samples of interest.

Lead cannot be analyzed using INAA. However, Pb can be measured in solid samples such as soils and sediments using GFAAS with slurry sampling [13]. With this approach, the detection limit for Pb in coals is reported to be on the order of 0.5 to 1 μg/g [14]. While this detection limit is comparable to that achieved using the EMMA instrument, the EMMA technique has the advantage of simultaneous determination of Cu, Zn, Br, Rb, and Sr in the peats, in addition to Pb.

Conclusions

The main advantage of the EMMA method over the conventional GFAAS method for measuring metals in solutions is that no sample dissolution is required for the EMMA analyses. This not only saves time, but also money because of the cost of high quality acids used for sample digestion, and the costs associated with microwave dissolution. Furthermore, the EMMA technique is not subject to matrix interferences; this latter point is especially important when measuring Pb by GFAAS in acid digests of peats from maritime bogs where sea salt chloride appears to have significantly suppressed the absorbance signal. While Pb can be measured in solid samples using GFAAS, the detection limits are no better than those reported here for EMMA. The EMMA technique, however, has the advantage of simultaneous determination of Cu, Zn, Br, Rb, and Sr in the peats, in addition to Pb.

The main disadvantage of the EMMA technique is the detection limit for Pb: while 0.3 μg/g is adequate for most peat samples from many kinds of bogs, in the samples taken from deeper, older sections (i.e. greater than approximately 3000 years b.p.) of ombrotrophic bogs, the pre-anthropogenic, natural "background" Pb concentrations are below this value. To accurately measure Pb in these samples, a more sensitive method is needed.

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