

Determination of Pb in the ash fraction of plants and peats using the Energy-dispersive Miniprobe Multielement Analyser (EMMA)

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Dry ashing at 550 °C was used to pre-concentrate Pb in peat and plant material prior to analysis using the Energy-dispersive Miniprobe Multielement Analyser (EMMA). Using approximately 1 g of starting material, precise determination of the ash content using a conventional laboratory balance (± 1 mg precision) was possible provided the mineral matter concentration exceeded about 3.5%, yielding approximately 35 mg of ash for analysis. To assess possible loss of Pb upon ashing, certified plant reference materials and independent analytical methods (ICP-MS of acid digests and EMMA analysis of whole peats) were used for comparison. No significant systematic loss of Pb occurred during ashing. The accuracy of Pb determinations using dry ashing was within 10% in plant materials containing as little as $0.5 \mu\text{g g}^{-1}$ (estimated from certified plant material). The EMMA determinations of Pb in peat by dry ashing generally agreed with the ICP-MS analyses of acid digests within 12% down to $0.2 \mu\text{g g}^{-1}$. The average limit of detection for a sample containing 2% of mineral matter was 100 ng g^{-1} , more than five times better than the detection limit obtained using EMMA analyses of whole peats. Overall accuracy and precision were better when Pb was measured by dry ashing compared to direct analysis of solid peats or plants.

The anthropogenic addition of Pb and other trace elements to the Earth ecosystems is recognised on a global scale.¹ To interpret the pollution of potentially toxic trace metals such as Pb, and their geochemistry in water, air, and soil, past historical perturbation as well as the current natural distribution in the Earth's biosphere have to be assessed fully.² While atmospheric deposition on plant surfaces allows the assessment of current pollution in urban and remote areas,^{3,4} ombrotrophic peat bogs act as archives of past anthropogenic and paleoclimatic perturbation reaching back thousands of years.^{5–7} The surface layers in ombrotrophic bogs receive their inorganic solids (typically below 15% ash) exclusively by atmospheric deposition. In older peat layers from pre-industrial times (pre-dating *ca.* AD 1800), Pb concentrations are generally low (down to $0.2 \mu\text{g g}^{-1}$)⁸ and require reliable, sensitive analytical methods.

The main multi-element analytical techniques used for Pb in peat are ICP-OES⁹ and XRF.^{10,11} ICP-OES is sensitive, but sample preparation can be a drawback as it is time consuming, involves expensive chemicals and is subject to the dangers of contamination. In addition, the complete acid dissolution of peat is difficult to achieve due to the complex inorganic and organic matrix.^{12,13} Energy dispersive X-ray spectrometry (ED-XRF) offers the opportunity of fast, non-destructive and inexpensive analysis and thus has widely been used for soils and sediments,^{14,15} coal,^{11,16} tree rings,^{17,18} plants,^{19,20} ash²¹ and peat bogs.^{10,20,22} A major drawback of commercial XRF instruments for analysing relatively 'clean' pre-industrial peat is, however, the high detection limits for Pb, generally a few $\mu\text{g g}^{-1}$ in solids.^{14,23}

To enrich Pb in organic and biological materials, dry digestion is often applied.^{24,25} Loss upon ashing at 550 °C is,

however, a reasonable concern,²⁴ especially for the non-mineral fraction of Pb (*i.e.*, organically bound, either exchangeable or complexed to the peat; most of 'anthropogenic' Pb is expected to be in this fraction). Lead is known to be conserved during ashing if it occurs as the sulfate, the nitrate, or the oxide phase, but if present as the chloride considerable care is required.²⁵ Also, the choice of the ashing crucible (ceramic, porcelain, silica, *etc.*) can be of prime importance. Retention losses due to the reaction of Pb with the solid matter of the crucible can occur. The most obvious reaction is between the oxide of the element of interest and the ashing vessel to produce a complex silicate, thereby causing a loss.^{24,25} Some oxides react much more readily than others, with lead oxide being one of the most reactive.²⁵ For biological materials including plant or food tissue, no significant difference between wet and dry ashing (450–550 °C) is usually found.^{26–28} For peats, however, literature data concerning possible losses are ambivalent, with some reports indicating no loss upon ashing at 550 °C,^{10,29,30} while others suggest occasional losses.^{31,32}

An Energy-dispersive Miniprobe Multielement Analyser (EMMA), originally designed and built for the geochemical analysis of single mineral grains^{33,34} and other small samples, has also been successfully applied to solid peats^{5,22} and soils.³⁵ The lower limit of detection for Pb in peat ($0.6 \mu\text{g g}^{-1}$) is approximately a factor of 10 better than commercial instruments.²³ However, in a peat core from western Switzerland (core 2p), representing 12 400 ¹⁴C years of peat accumulation, most samples older than *ca.* 3000 years contain less than $0.6 \mu\text{g g}^{-1}$ Pb. Clearly then, there existed a need for lowering the limit of detection with EMMA in peats.

The objectives of this study were therefore (i) to use the EMMA for measuring Pb in small volumes of plant and peat ash (≥ 35 mg), (ii) to enrich Pb in the ash fraction using dry ashing at 550 °C, thereby improving the limits of detection, (iii) to assess possible losses upon ashing (accuracy of the method),

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and (iv) to compare accuracy and precision of dry ashing with direct measurements in whole peats and plants.

Experimental

Sample description

Peat samples from cores of Scotland (6b) and Switzerland (2p, 2k) were used, all with different chemical matrix characteristics (e.g., various concentrations of ash, Cl or Br). The samples were mostly low in ash (<15%) and represent different periods of atmospheric Pb deposition (ages given in Table 1). The 2p core includes mainly pre-anthropogenic Pb concentrations, whereas 2k and 6b include Pb both from pre-industrial and recent times. The geochemistry of these deposits is described in more detail elsewhere.^{5,8,36} The plant samples used were all standard reference materials which included: Apple Leaves (NBS 1515), Pine Needles (NBS 1575) and Peach Leaves (NBS 1547) from the National Institute of Standards and Technology, USA; and Rye-Grass (CRM 281), Aquatic Plant (BCR 60) and Olive Leaves (BCR 62) from the European Community Bureau of Reference.

Sample preparation and measurement

Dry ashing was done as follows: one gram ($\pm 15\%$) of previously dried, milled and homogenised peat or plant material was placed in a pre-heated, acid washed porcelain crucible and dried again at 105 °C for 4 h. After 10 min cooling in a desiccator, the dry weight was determined to 1 mg. Ashing was accomplished by heating at 550 °C overnight. After cooling in the desiccator for 15 min the crucible was weighed again and the ash content calculated as weight per cent. The Pb concentration for the solid peat was calculated using the following equation: $c_{\text{solid peat}} = c_{\text{ash}} (\text{ash content}/100)$.

The Energy-dispersive Miniprobe Multielement Analyser (EMMA) used for the ash analysis is a small desk-top XRF system consisting of a conventional X-ray tube with Mo anode, focused LiF (200) wavelength monochromator, and rotating sample holder. Detection is accomplished with a 28 mm² Si(Li) detector. The spectrometer consists of a pulse amplifier, 12 bit Wilkinson analogue to digital converter, interface card and IBM compatible converter. Because monochromatic X-ray radiation is used for excitation ($\text{MoK}\alpha = 17.44 \text{ keV}$, $\lambda = 0.71 \text{ \AA}$), a low background is achieved. The schematic diagram of this ED-XRF spectrometer (Fig. 1) shows the set-up used for the ash analyses. The geometry avoids unnecessarily long beam paths with corresponding loss of X-ray intensity, and optimises the positioning of sample and detector. Approximately 35–100 mg of ash was placed into XRF Teflon sample cups (0.8 cm diameter) and placed in a sample holder. The sample thickness in the Teflon cups varied from 2 to 5 mm. This holder was rotated more than 400 times per analysis to compensate for sample inhomogeneity. A conventional optical microscope was used to view and centre the sample. The exiting $\text{K}\alpha$ beam was collimated by a conical compact slit of dimensions $2 \times 0.7 \text{ mm}$. The X-ray tube was operated at a voltage of 30 kV and a current of 5 mA. Each spectrum was recorded for 1200 s. The

calibration standards³⁷ used for the elemental analysis of ashed peat were: certified rock reference materials of the US Geological Survey—Diabase W-1, Andesite AGV-1, Basalt BCR-1, Granite G-2, and Peridotite PCC-1; and an artificial glass standard of the Association Nationale de la Recherche Technique (ANRT) from France—VS-N. Using natural certified reference materials has the advantage of matrix-matching with the samples. A calibration procedure using analytical line intensity *versus* concentration is likely to be incorrect for the analysis of ash³⁴ due to its inhomogeneous surface, different sample geometry or the varying mean mass attenuation coefficients of ashed peat, plant and rock samples. Thus, to standardise internally, the elemental peaks were normalised to the area of the incoherent Compton scattering.³⁸ The incoherent : coherent ratio for ashed samples and rock standards were almost the same, implying that the mass absorption coefficients (MAC) were almost the same for all analysed samples and very close to the MAC for rock standards. The concentrations of Pb in the certified materials ranged from 7.8 to 950 $\mu\text{g g}^{-1}$ and the correlation coefficient for the normalised peak area *versus* concentration was >0.999 .

EMMA analyses of Pb in whole peats are described in detail elsewhere.²²

Quantitative ICP-MS analyses of Pb were carried out using a Perkin-Elmer ELAN 5000 (SCIEX, Thornhill, ON, Canada). About 250 mg of the dried sample were placed in Teflon bombs. Digests were carried out using 4 ml concentrated HNO_3 (65%) + 3 ml concentrated H_2O_2 (30%) + 1 ml concentrated HF (40%). All reagents used were of Merck Suprapur quality (E. Merck, Darmstadt, Germany). The bombs were sealed and digested using several subsequent cycles with different power: 5 min at 250 W, 6 min at 600 W, 4 min at 450 W, 4 min at 350 W, 5 min at 250 W and vent for 30 min. The microwave system employed was a low pressure MLS 1200 microwave digestion system (Milestone S.R.L., Hitzkirch, Germany).¹² Operational blanks consisted of the acids reacted in the Teflon bombs without any solid sample material and were all below limit of detection. For the ICP-MS measurements, the digestion solutions were diluted 1 + 9 ml with 18 M Ω H_2O . In Table 2, the experimental conditions and operating parameters for the ICP-MS are given. Pb was quantified using an external calibration. The acid matrix was adjusted for the calibration solution. A six point calibration was done for the range of 0.5–100 ng ml⁻¹. To control matrix effects due to varying concentrations of dissolved salts or acids, selected samples were determined with standard addition using

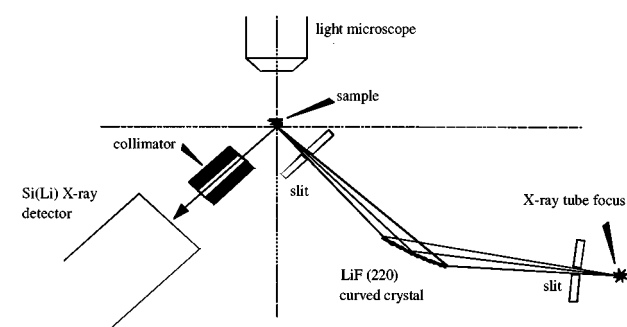


Fig. 1 Schematic drawing of the Energy-dispersive Miniprobe Multi-Element Analyser (EMMA). From Cheburkin *et al.*³⁴

Table 1 Selected characteristics of the investigated peats

| Peat core | Origin | Reference | Ash (%) | Time period/yr BP ^a | Depth/cm |
|-----------|--------------------------|-------------|----------|--------------------------------|----------|
| 2k | Switzerland, continental | Unpublished | 1.4–6.9 | Present–ca. 2000 ^b | 0–100 |
| 2p | Switzerland, continental | Ref. 6, 8 | 1.0–14.4 | ca. 2100–ca. 12 370 | 100–650 |
| 6b | Scotland, maritime | Ref. 36 | 2.8–25.2 | Present–ca. 1200 ^b | 0–100 |

^a yrs BP = ¹⁴C years before AD 1950, dated by ¹⁴C decay counting. See Weiss *et al.*,⁸ for details. ^b Based on the age dates from a replicated core.

the ICP-MS multielement standard IV reference solution from Merck. Three spikes were used (ranging from 0.25–25 ng ml⁻¹) and the results agreed very well. The analytical precisions for Pb for different concentration ranges of solid peats and SRM were: $\pm 10\%$ ($< 0.25 \mu\text{g g}^{-1}$); $\pm 8\%$ ($0.25\text{--}0.8 \mu\text{g g}^{-1}$); $\pm 6\%$ ($0.8\text{--}1.0 \mu\text{g g}^{-1}$); $\pm 5\%$ ($1.0\text{--}5.0 \mu\text{g g}^{-1}$); and $\pm 3\%$ ($> 5.0 \mu\text{g g}^{-1}$). The accuracy was determined by multiple measurements of the certified material Apple Leaves (NBS 1515), Peach Leaves (NBS 1547) and Pine Needle (NBS 1575) and was within 10%.

Results and discussion

Precision of ashing

As dry ashing introduces an additional analytical step, the precision of the ashing procedure itself for plant and peat material required assessment. The initial amount of sample utilised was 1000 ± 150 mg. The balance used was a typical, top-loading electronic laboratory balance.³⁹ Selected peat and plant samples with ash concentrations ranging from 1.5 to 21%, yielding a final mass of 17 to 270 mg of ash, were ashed six times and the error was expressed as the relative standard deviation (RSD). As can be seen in Table 3, samples with ash concentrations above 2% yielded good reproducibility and the errors were at or below 3%. The relatively high error of 12% in sample 2p10 (yielding 17 mg of ash), is partly a reflection of the error associated with the balance itself (± 1 mg). For better precision using low ash peats or plants, either a more sensitive analytical balance is needed (*e.g.*, a microanalytical balance) to

weigh the ash, or more dry peat (*e.g.*, 2 g) must be combusted. With the conventional balance used in this study, final masses lower than 35 mg were not used for further analysis.

Accuracy

To assess possible losses of Pb upon ashing plant materials and thus the accuracy of the method, certified plant standard reference materials (SRM) were ashed. As can be seen in Table 4, the recoveries were good for Pb, ranging between 96 and 117% for a wide range of Pb concentrations ($0.47\text{--}63.5 \mu\text{g g}^{-1}$) and ash contents (2.6–21%). This suggests that there were no significant losses of Pb upon ashing by retention or volatilisation, and supports the use of ashing as a reliable method to concentrate Pb in plants.²⁷

Unfortunately, there are no certified reference materials for peat to assess the accuracy of Pb preconcentration by ashing. To evaluate possible losses during the ashing of peats, we compared elemental Pb concentrations obtained by dry ashing with (i) ICP-MS analysis of acid digests of core 2p and core 2k, and (ii) EMMA analysis of whole peats from core 6b. The EMMA analyses of whole peats (*y*) are in good agreement with the values obtained by analysing the corresponding ash samples (*x*) with $y = 1.001x - 0.213$ ($r^2 = 0.992$, $n = 30$) for core 6b (Fig. 2). The ICP-MS results for the cores 2p and 2k are slightly higher than the values obtained by EMMA analyses of peat ash (Fig. 2). In core 2p, there are two samples with significantly higher values using ICP-MS, possibly indicating either a loss of Pb upon ashing or, more likely, a slight contamination problem in the acid digest. However, given the linear regressions (Fig. 2), the estimated overall precision with a standard error of $< 12\%$ for the analyses by dry ashing is acceptable. This error is well within the precision range of the EMMA measurements of ashed peat and the ICP-MS measurements of acid digests¹² of low concentration ranges. In summary, for Pb in the concentration range of $0.2\text{--}100 \mu\text{g g}^{-1}$ in solid peat and 0.5 to $63 \mu\text{g g}^{-1}$ in solid plants, there occurred no significant loss upon ashing.

Lead in core 2p and the lower parts of 2k and 6b is probably hosted mainly in silicates^{12,40} compared with the upper parts of core 2k and 6b, where organically bound, anthropogenic Pb probably dominates.^{36,40} Therefore, the results presented here suggest that Pb is conserved during ashing, regardless of the chemical form in which it is present. This agrees with previous investigations,^{29,41} which compared dry ashing and wet digestion of recent peats.

Precision

To investigate the overall reproducibility of Pb analyses by dry ashing, seven peat samples with low ($1.2\text{--}5.2 \mu\text{g g}^{-1}$) and high

Table 2 Experimental conditions and operating parameters for the ICP-MS

| | | |
|----------------------|----------------------------|--------------------------|
| Instrument | ICP-MS ELAN (Perkin-Elmer) | |
| Nebulizer | Meinrad concentric glass | |
| Spray chamber | Glass | |
| Gas flows (Ar) | Nebulizer | 1.0 l min ⁻¹ |
| | Auxiliary | 0.8 l min ⁻¹ |
| | Cool | 15.0 l min ⁻¹ |
| Cones | Sampler | Platin |
| | Skimmer | Platin |
| Dwell time | 300 ms | |
| Sweeps/reading | 5 | |
| Readings/replicate | 1 | |
| Number of replicates | 5 | |
| Points across peak | 1 | |
| Scanning mode | Peak hopping | |
| Plasma power | 1000 W | |
| Magnet mass | 208 | |
| Analysis time | 3.5 min | |

Table 3 Precision of ashing using 1000 ± 150 mg starting material. Precision of balance ± 1 mg. Error is the standard deviation based on 6 determinations

| Material | Sample ID# | Amount ash left after ashing/mg | Ash (%) | <i>s</i> ($\pm 1\sigma$) | RSD (%) |
|----------|------------------------|---------------------------------|---------|----------------------------|---------|
| Peat | 2k11 | 45 | 4.57 | 0.08 | 2 |
| | 2k12 | 49 | 4.72 | 0.12 | 3 |
| | 2p10 | 17 | 1.49 | 0.18 | 12 |
| | 2p44 | 167 | 14.92 | 0.10 | 1 |
| | 6b13 | 83 | 4.68 | 0.10 | 2 |
| | 6b15 | 43 | 5.00 | 0.15 | 3 |
| | 6b81 | 82 | 8.63 | 0.27 | 3 |
| | 6b83 | 97 | 9.95 | 0.21 | 2 |
| | NIST 1547 Peach-Leaves | 116 | 9.59 | 0.08 | 1 |
| Plant | NIST 1515 Apple-Leaves | 89 | 7.46 | 0.09 | 1 |
| | NIST 1575 Pine-Needles | 35 | 2.60 | 0.04 | 1 |
| | BCR 62 Olive-Leaves | 80 | 6.32 | 0.11 | 2 |
| | BCR 60 Aquatic Plant | 270 | 21.17 | 0.17 | 1 |
| | BCR 281 Rye Grass | 113 | 9.63 | 0.07 | 1 |

(68.8–77.2 $\mu\text{g g}^{-1}$) concentrations were ashed six times each and the Pb concentrations determined. To compare with EMMA measurements in solid peat, eight additional samples with similarly high and low Pb concentrations were also measured. As can be seen in Table 5, the precision was satisfactory with relative standard deviation of $\leq 14\%$ down to 1.2 $\mu\text{g g}^{-1}$ using dry ashing (2p10), and down to 2.5–3.7 $\mu\text{g g}^{-1}$ using direct measurement of solid samples (2k20 and 6b82, respectively). At high Pb concentrations, the precision of the two methods is

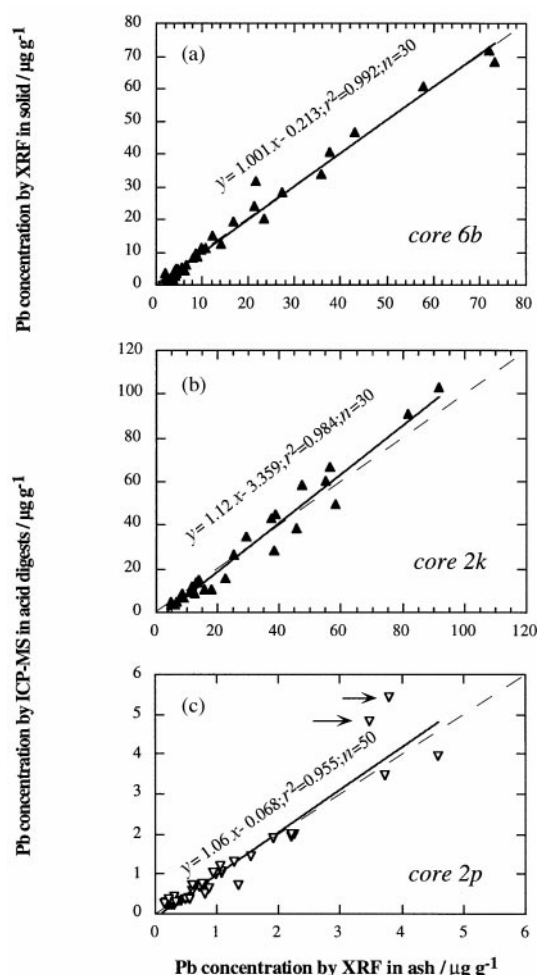


Fig. 2 Scatter diagrams of Pb obtained using: (a) EMMA of whole peat versus peat ash in core 6b; (b) ICP-MS versus peat ash in core 2k; (c) ICP-MS versus peat ash in core 2p with two outliers indicated by arrows (see text for details). The broken line is the 1 : 1 line of equivalence.

similar. In the lower concentration ranges ($\leq 2 \mu\text{g g}^{-1}$ Pb), however, the precision of the Pb determinations seems improved by dry ashing (comparing, for example, sample 2p10 with a relative standard deviation of 14% using dry ashing and of 30% using direct analysis of solid peat). In certified plant reference materials, low Pb concentrations showed an even better reproducibility upon dry ashing (Table 4).

In summary, the reproducibilities of Pb measured by dry ashing and directly in solid peat are similar in the higher concentration ranges. In the lower concentration ranges ($\leq 2 \mu\text{g g}^{-1}$ Pb), however, the reproducibility of the Pb measurements was improved by dry ashing. Thus, no additional sample heterogeneity is introduced by ashing and the small sample size (down to 35 mg) used for the analysis.

In Fig. 3, three Pb concentration profiles of the whole 2p peat core are shown. The core extends from 100 to 650 cm deep and corresponds to the period from 12 400 to ca. 2000 ^{14}C yrs BP. To assess the precision, Pb was measured twice in the ash fraction with EMMA and all measurements agreed to within 15%. Lead measurements obtained using EMMA were also in good agreement with the ICP-MS values (within 12% on average). Features such as the Pb peaks (#1–3) indicated in Fig. 3 are clearly seen using both analytical methods. Peak #3 shows a significant disagreement, possibly indicating some contamination of the acid digest analysed using ICP-MS (see also Fig. 2c and discussion above).

Table 5 Reproducibility of Pb determination by dry ashing (a) and direct measurement in solid peat (b). Error is the relative standard deviation based on six determinations. n.d. = not determined

| Sample | Ash (%) | Pb concentration (ppm) | RSD (%) |
|-------------------------|---------|------------------------|---------|
| (a) Ashed peat samples— | | | |
| 2k11 | 4.6 | 77.2 | 3 |
| 2p10 | 1.5 | 1.2 | 14 |
| 2p44 | 14.9 | 5.2 | 6 |
| 6b13 | 4.7 | 69.4 | 2 |
| 6b14 | 5.0 | 68.8 | 2 |
| 6b81 | 8.6 | 3.2 | 8 |
| 6b83 | 10.0 | 4.6 | 8 |
| (b) Whole peat samples— | | | |
| 2k10 | 2.8 | 62.8 | 2 |
| 2k20 | 3.8 | 2.5 | 14 |
| 2k30 | 1.8 | 10.2 | 5 |
| 2p10 | 1.5 | 1.5 | 30 |
| 6b16 | n.d. | 80.0 | 2 |
| 6b18 | n.d. | 57.2 | 2 |
| 6b82 | n.d. | 3.7 | 14 |
| 6b84 | n.d. | 4.5 | 11 |

Table 4 Pb recovery of certified standard reference materials after dry ashing of 1000 ± 150 mg plant at 550 $^{\circ}\text{C}$

| Sample ID# | Ash (%) | Pb measured in ash (ppm) | Pb certified (ppm) | Pb calculated in plant (ppm) | Recovery (%) |
|--------------------------|---------|--------------------------|--------------------|------------------------------|--------------|
| NIST 1515 Apple-Leaves 1 | 7.4 | 7.3 | 0.47 | 0.54 | 115 |
| NIST 1515 Apple-Leaves 2 | 7.6 | 7.0 | 0.47 | 0.53 | 113 |
| NIST 1515 Apple-Leaves 3 | 7.4 | 7.0 | 0.47 | 0.52 | 110 |
| NIST 1575 Pine-Needles 1 | 2.6 | 421.6 | 10.8 | 11.12 | 103 |
| NIST 1575 Pine-Needles 2 | 2.6 | 397.2 | 10.8 | 10.37 | 96 |
| NIST 1575 Pine-Needles 3 | 2.6 | 408.9 | 10.8 | 10.48 | 97 |
| BCR 62 Olive-Leaves 1 | 6.3 | 368.1 | 25 | 23.31 | 93 |
| BCR 62 Olive-Leaves 2 | 6.4 | 424.5 | 25 | 27.29 | 109 |
| BCR 62 Olive-Leaves 3 | 6.2 | 411.8 | 25 | 25.56 | 102 |
| BCR 60 Aquatic Plant 1 | 21.1 | 351.5 | 63.5 | 74.15 | 117 |
| BCR 60 Aquatic Plant 2 | 21.0 | 340.1 | 63.5 | 71.57 | 113 |
| BCR 60 Aquatic Plant 3 | 21.4 | 338.8 | 63.5 | 72.38 | 114 |
| BCR 281 Rye Grass 1 | 9.7 | 25.2 | 2.38 | 2.44 | 103 |
| BCR 281 Rye Grass 2 | 9.7 | 29.4 | 2.38 | 2.84 | 117 |
| BCR 281 Rye Grass 3 | 9.6 | 28.6 | 2.38 | 2.73 | 115 |

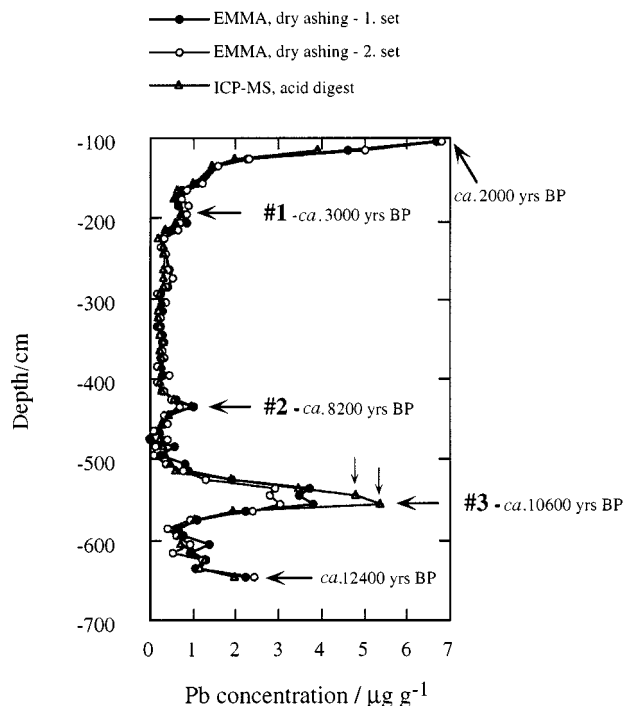


Fig. 3 Pb concentrations in peat profile 2p from Switzerland, representing atmospheric Pb deposition from 12 400 until *ca.* 2000 yrs BP. Pb values were obtained using EMMA analyses in ash (two sets of measurements) and using ICP-MS analyses in acid digests of the same samples. For most of these samples, Pb measured directly in whole peats was below the LOD using EMMA. The peaks #1, #2 and #3 denote features in the profile which are particularly important for paleoclimate, archaeological and environmental studies (see Shoty *et al.*⁶ and Weiss *et al.*⁸ for details). The corresponding ages are shown in conventional ¹⁴C yrs BP.

Table 6 Limits of detection for Pb in the rock and plant standards

| Standards | Average LOD ^a (ppm) | Range of LOD ^b (ppm) | Concentration range of investigated standards (ppm) |
|-----------|--------------------------------|---------------------------------|---|
| Rock | 5.2 | 3.0–7.4 | 7.8–950 |
| Plant | 1.8 | 0.6–2.6 | 0.87–63.8 |

^a Average of calculated LOD from 5 standards (see text for details).

^b Each limit of detection (LOD) is based on the average of individual standards measured in triplicate.

Limit of detection (LOD)

The limit of detection (LOD) for Pb was calculated as $LOD = 3c(N_b)^{0.5}/N_p$, where N_b is the number of counts in the background, N_p is the number of counts in the characteristic peak of the analyte element and c is the certified elemental concentration in the analysed material.¹⁷ The detection limits for peat and plant ash and solid were calculated using triplicate analysis of five different certified standard reference materials for both rock certified reference materials (taken to represent peat ash) and plant certified reference materials. The calculated detection limits are a function of the concentration of Pb in the standard reference material and its matrix. The range of calculated LODs varied from 0.6 to 2.6 $\mu\text{g g}^{-1}$ for plant material and 3.0–7.4 $\mu\text{g g}^{-1}$ for rocks (Table 6). The lower LODs for rocks and plants (3.0 and 0.6 $\mu\text{g g}^{-1}$ Pb, respectively) are in good agreement with previous EMMA analyses of solid peat³⁴ and mineral material.²²

The lower LOD for Pb in the rock certified reference materials is 3.0 $\mu\text{g g}^{-1}$, compared with 0.6 $\mu\text{g g}^{-1}$ for the plant certified reference materials. The average LOD values are 5.2 $\mu\text{g g}^{-1}$ and 1.8 $\mu\text{g g}^{-1}$ for rock and plant certified reference

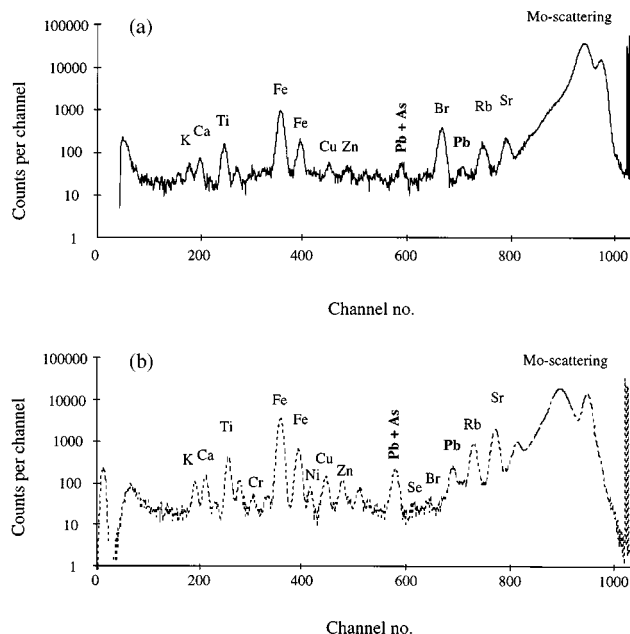


Fig. 4 X-ray fluorescence spectrum of sample 2k20, containing $2.5 \pm 0.3 \mu\text{g g}^{-1}$ Pb, in (a) solid peat and (b) ashed peat. Note the improved signal to noise ratios using the peat ash and the low background intensity.

materials, respectively. However, during ashing, Pb and other conservative trace elements are concentrated, with the enrichment factor dependent on the ash content. For example, in a peat or plant sample containing 2% ash (typical of ombrotrophic peats used for paleoclimatic constructions), conservative elements are enriched 50-fold during dry ashing. Thus, the average LOD for Pb in peat ash yields an average LOD in the whole peat of 0.10 $\mu\text{g g}^{-1}$ and a lower LOD of 0.06 $\mu\text{g g}^{-1}$. Compared to the lower LOD for Pb in whole peat by EMMA which is 0.6 $\mu\text{g g}^{-1}$ (Table 6), the LOD values for peat ash are 6–10 times better.

In Fig. 4, the X-ray fluorescence spectrum of sample 2k20 ($\text{Pb} = 2.5 \pm 0.3 \mu\text{g g}^{-1}$) in (a) solid peat and (b) ashed peat is shown. In ashed peat, the Pb peaks ($L\alpha$ and $L\beta$ emission lines) are significantly greater, resulting in higher counting statistics and therefore a lower analytical error for the same concentration range. In addition, the peaks for a number of other elements of interest also are considerably improved (Cu, Zn). Some elements, such as Cr and Ni, are below the LOD in whole peats, but above the LOD in peat ash. Thus, for refractory elements, pre-concentration by dry ashing offers significantly improved limits of detection in peats and plants. Volatile elements such as Br (boiling point of 59 °C), however, are lost during ashing. Note also that the background intensity is low compared to other XRF analyses of ash²¹ because monochromatic X-ray radiation was used for excitation ($\text{Mo-K}\alpha = 17.44 \text{ keV}$, $\lambda = 0.71 \text{ \AA}$).

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References

- 1 W. S. Fyfe, *Science (Washington D.C.)*, 1981, **213**, 105.
- 2 J. O. Nriagu, *Science (Washington D.C.)*, 1996, **272**, 223.

- 3 H. R. Ross, *Water, Air, Soil Pollut.*, 1990, **50**, 63.
- 4 J. Carignan and C. Gariépy, *Geochim. Cosmochim. Acta*, 1995, **59**, 4427.
- 5 W. Shotyk, A. K. Cheburkin, P. G. Appleby, A. Fankhauser and J. D. Kramers, *Earth Planet. Sci. Lett.*, 1996, **145**, E1.
- 6 W. Shotyk, D. Weiss, P. G. Appleby, A. K. Cheburkin, R. Frei, M. Gloor, J. D. Kramers, S. Reese and W. O. van der Knaap, *Science*, (Washington D.C.), 1998, **281**, 1635.
- 7 M. L. Bränvall, R. Bindler, O. Emteryd, M. Nilsson and I. Renberg, *Water, Air, Soil Pollut.*, 1997, **100**, 243.
- 8 D. Weiss, W. Shotyk, A. K. Cheburkin, M. Gloor and S. Reese, *Water, Air, Soil Pollut.*, 1997, **100**, 311.
- 9 B. Markert and I. Thornton, *Water, Air, Soil Pollut.*, 1990, **49**, 113.
- 10 M. Görres and B. Frenzel, *Naturwissen.*, 1993, **80**, 333.
- 11 J. P. Willis, *A Comparison of Trace Element Analysis of Whole Coal by INAA and XRFs*, CSI-Symposium CSI XXIV, Jülich, 1986, Jül-Conf-55, 101–110.
- 12 D. Weiss, W. Shotyk, J. Schäfer, U. Loyall, E. Grolimund and M. Gloor, *Fresenius' J. Anal. Chem.*, in the press.
- 13 C. S. E. Papp and L. B. Fischer, *Analyst*, 1987, **112**, 337.
- 14 L. Vogel-Kopplitz, J. Urbanik, S. Harris and O. Mills, *Environ. Sci. Technol.*, 1994, **28**, 538.
- 15 P. Wilson, M. Cooke, J. Cawley, L. Giles and M. West, *X-ray Spectrom.*, 1995, **24**, 103.
- 16 J. P. Willis, in *X-ray Fluorescence Analysis in the Geological Sciences—Advances in Methodology*, ed. S.T. Ahmedali, Geological Association of Canada, Montreal, Quebec, Canada, 1989, Short Course 7, pp. 91–110.
- 17 J. Boman, C. Larsson, M. Olsson and H. Raitio, *X-ray Spectrom.*, 1996, **25**, 89.
- 18 A. Rindby, *X-ray Spectrom.*, 1993, **22**, 187.
- 19 E. Selin, P. Standzenieks, J. Boman and V. Teeyasoontranont, *X-ray Spectrom.*, 1993, **22**, 281.
- 20 J. Omote, H. Kohno and K. Toda, *Anal. Chim. Acta*, 1995, **307**, 117.
- 21 V. Vijayan, S. N. Behera, V. S. Ramamurthy, S. Puri, J. S. Shahi and N. Singh, *X-ray Spectrom.*, 1997, **26**, 65.
- 22 A. K. Cheburkin and W. Shotyk, *Fresenius' J. Anal. Chem.*, 1996, **354**, 688.
- 23 J. P. Willis, *Fresenius' Z. Anal. Chem.*, 1986, **324**, 855.
- 24 T. T. Gorsuch, *Analyst*, 1959, **84**, 135.
- 25 T. T. Gorsuch, *The Destruction of Organic Matter*, Pergamon Press, London, 1970.
- 26 Z. Xue and Y. Wang, *J. Radioanal. Nucl. Chem. Lett.*, 1987, **119**, 425.
- 27 P. Mader, J. Szàková and E. Curdova, *Talanta*, 1996, **43**, 521.
- 28 S. B. Adeloju, *Analyst*, 1989, **114**, 455.
- 29 C. S. E. Papp and T. F. Harms, *Analyst*, 1985, **110**, 237.
- 30 N. Müller and N. Lambersdorf, *Telma*, 1995, **25**, 143.
- 31 M. W. Ali, S. C. Zoltai and F. G. Radford, *Can. J. Soil Sci.*, 1988, 443.
- 32 W. A. Glooschenko, J. A. Capobianco, T. Mayer and M. Gregory, *Proceedings of the 6th International Peat Congress, Minnesota, USA*, International Peat Society, 1979, 551–555.
- 33 A. K. Cheburkin, A. V. Andreyev and V. V. Demyanenko, *Geol. Geofiz.*, 1988, **8**, 47.
- 34 A. K. Cheburkin, R. Frei and W. Shotyk, *Chem. Geol.*, 1997, **135**, 75.
- 35 W. Shotyk, A. K. Cheburkin and A. V. Andreyev, in *Proceedings of the 9th International Conference on Heavy Metals in the Environment, Toronto, Canada*, CEP Consultants, Edinburgh, UK, 1993, **1**, 175–179.
- 36 W. Shotyk, *Chem. Geol.*, 1997, **138**, 55.
- 37 K. Govindaraju, *Geostand. Newsl.*, 1989, **13**, 1.
- 38 R. M. Rousseau, J. P. Willis and A. R. Duncan, *X-ray Spectrom.*, 1996, **25**, 179.
- 39 D. C. Harris, *Quantitative Chemical Analysis*, W. H. Freeman and Company, New York, USA, 2nd edn., 1992.
- 40 D. Weiss, PhD Thesis, University of Bern, Switzerland, 1998.
- 41 W. A. Glooschenko, in *Toxic metals in the Atmosphere*, ed. J. O. Nriagu and D. I. Davidson, John Wiley and Sons, New York, USA, 1986, pp. 57–64.

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