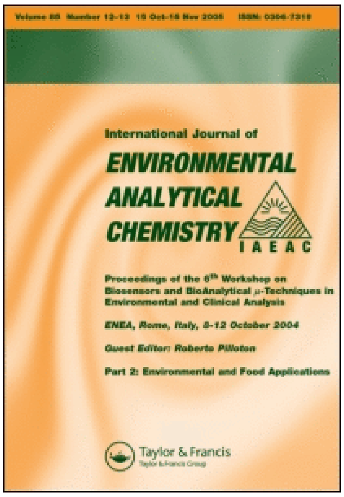

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Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma/Mass Spectrometry (ICP-MS) for Trace Element Biomonitoring using Mosses

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INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA) AND INDUCTIVELY COUPLED PLASMA/MASS SPECTROMETRY (ICP-MS) FOR TRACE ELEMENT BIOMONITORING USING MOSSES

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Two analytical methods – instrumental neutron activation analysis (INAA) and inductively coupled plasma mass spectrometry (ICP-MS) – were used for the trace element analysis of naturally growing mosses for a heavy metal biomonitoring survey. The techniques were applied to reference mosses to evaluate the feasibility, analytical variability, detection limits and accuracy. These parameters were evaluated using 563 mosses sampled in the 1996 French survey.

All the elements of interest in the European program "Atmospheric Heavy Metal Deposition in Europe – estimation based on moss analysis" (As, Cd, Cr, Cu, Fe, Hg, Pb, Ni, V, Zn) were able to be determined by ICP-MS. INAA appeared suitable for the determination of As, Cr, Fe, Hg, V and Zn. The Cd, Cu, Ni and Pb concentrations determined by ICP-MS were preferred to the INAA results, because of increased feasibility or accuracy.

The results provided by both methods on the French mosses were statistically compared for 14 elements. Significant linear correlation appeared for: Ba, Ce, Cs, La, Rb, Sm, Th and V. Among these eight elements, Ba, Cs, La and Sm concentrations determined by both methods exhibited a strong statistical similarity. The correlations obtained for As, Eu, Fe and Sb were not as strong and no correlation at all was observed for Co and Cr. These differences were attributed to instrumental factors (e.g. spectral interference occurred for both methods) or due to the sample preparation prior to ICP-MS. The consequences of such results on the regional trend evaluation of atmospheric heavy metal deposition were discussed.

Keywords: Biomonitoring; Mosses; Trace elements; Elemental analysis; INAA; ICP-MS

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INTRODUCTION

Since the earlier investigations in 1968 [1], mosses have been increasingly used as biomonitors in atmospheric deposition studies. The European program "Atmospheric Heavy Metal Deposition in Europe – estimation based on moss analysis" concerns ten elements: As, Cd, Cr, Cu, Fe, Hg, Pb, Ni, V, Zn [2]. The first French contribution [3] to this program provides information about the atmospheric deposition of 36 trace elements in 563 naturally growing mosses sampled throughout France. It was decided to investigate a large number of elements: Al, As, Au, Ba, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Eu, Fe, Hg, I, K, La, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sc, Se, Sm, Th, Ti, V, W, Zn and Zr, including toxic metals, like Sb, and lithophilic elements, such as the Rare Earth elements and Ba, in order to provide information on the influence of elements issued from soil dusts. Several publications have described the abilities of mosses to be used as biomonitors of atmospheric pollution [4–9] and many have reported their results in a spatial dimension [2,9–11]. Various methods (INAA, XRF, ICP-AES, ICP-MS and AAS), characterized by different limitations (number of elements determined simultaneously, preparation steps), exist for moss analysis [12]. Among them, ICP-MS is the most promising analytical method [13] for such biomonitoring studies realizing a large number of samples and elements of interest. INAA, with a very different physical principle, appears to remain a reference method in trace element analysis for the environment [14,15].

Both methods have been applied to the analysis of 563 mosses sampled in France [16]. The present article highlights the analytical methodology of this survey, from sample preparation to data selection for map drawing. It aims to supply practical information on INAA and ICP-MS feasibility, accuracy and precision in multielement studies using mosses as biomonitors. The analytical procedures are evaluated for a large range of elements using two intercalibrated mosses. The impact of both methods on international biomonitoring studies is discussed in light of statistical comparisons between both data sets.

EXPERIMENTAL

Materials

Five mosses species were used, from the more to the less frequently sampled: *Hypnum cupressiforme, Scleropodium purum, Pleurozium schreberi* and *Hylocomium splendens*. The choice of species and the sampling methods followed the European guideline [2]. The samples were dried at 40°C and manually homogenized in an agate mill.

Methods

INAA: The samples were mixed with 60 mg of ultra-pure cellulose powder and prepared in the form of pellets. Each pellet was sealed in a polyethylene bag (short irradiation) or wrapped in ultra-pure aluminum foil (long irradiation). Irradiations were performed using the CEA/Saclay Orphee reactor (thermal neutrons). One-minute irradiation under $1.3 \times 10^{13}\,\mathrm{n\,cm^{-2}\,s^{-1}}$ flux was used for the determination of elements with short half-life isotopes, from 2.3 min (^{28}Al) to 15 h (^{24}Na).

Two counting periods were performed immediately after irradiation: 2 and 15 min. Seventeen-hours irradiation ($2.3 \times 10^{13}\,n\,cm^{-2}\,s^{-1}$) allowed the determination of longer half-life isotopes, from 15 h (^{24}Na) to 13 years (^{152}Eu). Two counting sequences were performed: for 2 h after 4-days cooling and for 5 h after 15 days. The K_0-method was applied using the k0Labsue software [17]. The radioisotopes that were measured and the γ-energy monitored are detailed in Table I.

ICP-MS: The analytical procedure has been described in a previous paper [18]. An amount of 50–70 mg of sample was digested in a microwave oven in PTFE vessels with 5 ml of HNO_3, 5 ml H_2O_2, 5 ml HF, 3 ml HNO_3 and 10 ml H_2O. The ICP-MS analyses were performed using a quadrupole VG Plasmaquad II+ (VG Elemental, Cheshire, UK).

Reference Materials

Two mosses, from the three moss samples prepared for an inter-laboratory comparison [19] were analyzed regularly, according to the procedures used for French moss

TABLE I Experimental conditions for instrumental neutron activation analysis

Element	*Radio-isotope*	*Irradiation time*	*Cooling time*	*Gamma ray energies used* (keV)
Ag	^{110m}Ag	17 h	15 d	657.7
Al	^{28}Al	1 min	5 min	1778.9
As	^{76}As	17 h	4 d	559.1
Ba	^{131}Ba	17 h	15 d	496.3
Br	^{82}Br	17 h	4 d	776.5
Ca	^{47}Sc	17 h	4 d	159.4
Cd	^{115m}In	17 h	4 d	336.2
Ce	^{141}Ce	17 h	15 d	145.4
Cl	^{38}Cl	1 min	15 min	1642.4–2167.5
Co	^{60}Co	17 h	15 d	1173.2–1332.5
Cr	^{51}Cr	17 h	15 d	320.1
Cs	^{134}Cs	17 h	15 d	604.7
Cu	^{66}Cu	1 min	5 min	1039.2
Fe	^{59}Fe	17 h	15 d	1099.3–1291.6
Ga	^{72}Ga	17 h	4 d	834.0
Hg	^{203}Hg	17 h	15 d	279.2
K	^{42}K	17 h	4 d	1524.7
La	^{140}La	17 h	4 d	487.0
Mg	^{27}Mg	1 min	5 min	1014.4
Mn	^{56}Mn	1 min	15 min	846.8
Mo	^{99}Tc	17 h	4 d	140.5
Na	^{24}Na	17 h	4 d	1368.6
Rb	^{86}Rb	17 h	15 d	1076.8
Sb	^{122}Sb	17 h	4 d	564.1
Sc	^{46}Sc	17 h	15 d	1120.5
Se	^{75}Se	17 h	4 d	264.7
Sm	^{153}Sm	17 h	4 d	103.2
Sr	^{85}Sr	17 h	15 d	514.0
Th	^{233}Pa	17 h	15 d	312.0
Ti	^{51}Ti	1 min	15 min	320.1
U	^{239}Np	17 h	4 d	228.2
V	^{52}V	1 min	5 min	1434.7
W	^{187}W	17 h	4 d	685.7
Zn	^{65}Zn	17 h	15 d	1115.6
Zr	^{95}Zr	17 h	15 d	756.7

analyses, rather than the procedures recommended for the inter-calibration, as a check for accuracy and precision. In particular, the sample weights were decreased from 500 to 70 mg to minimize the gamma activities produced by irradiation (INAA) and the reagent quantities necessary for complete digestion (ICP-MS).

RESULTS AND DISCUSSION

Feasibility of INAA and ICP-MS for Trace Determination in Mosses

Multiple irradiation, cooling and counting times were used. Thus, INAA allowed the determination of 34 elements using two 70 mg portions. Al, Cl, Cu, I, Mg, Mn, Ti and V were determined with short irradiations. Long irradiations provided information about: As, Au, Ba, Br, Ca, Cd, Ce, Co, Cr, Cs, Eu, Fe, Hg, K, La, Mo, Na, Rb, Sb, Sc, Se, Sm, Sr, Th, W, Zn and Zr. In the conditions used, Ni was not determined. A third irradiation with fast neutrons would be necessary to determine Ni, however, difficulties may arise from the irradiation of organic materials with an intense neutron flux. Pb is not measurable by Neutron Activation. Thus, these two later elements, which are of key interest in air pollution studies, were not determined by INAA. ICP-MS, theoretically, covers all the elements of interest. In practice, isobaric interferences with the plasma gas – Argon, prevent the determination of some elements (e.g. K, Br). Twenty-four elements were retained for ICP-MS: As, Ba, Bi, Cd, Ce, Co, Cr, Cs, Cu, Fe, Hg, La, Mo, Ni, Pb, Rb, Sb, Sc, Sr, Th, Tl, Ti, U, V and W. Due to the high and variable blank values of Zn when using the flasks at the beginning of this work, this metal was not determined by ICP-MS. Further tests with different flasks showed that Zn determination by ICP-MS in mosses was feasible.

Analytical Variability

The results obtained on the inter-calibrated mosses M1 and M2 were used to evaluate the error associated to the French mosses analyses. The relative standard deviations (RSD) were in the same order for M1 and M2. For the ten elements of interest to the European program, the INAA variability, due to the activation and gamma spectrometry, is 5–20%. For ICP-MS, Cu, Pb, Rb, Sr and V, RSD values were less than 10%, equal to 10% for Ba, Bi, Cd, Cs, La and Sm and between 10 and 20% for As, Ce, Co, Cr, Eu, Fe, Mo, Ni, Sb, Th, Tl, U and W. The larger RSD values may be attributed to a larger variability when using 70 mg samples, compared to 500 mg portions. Four replicates of 30, 50, 75, 100, 150, 200 and 300 mg portions were analyzed (M1 and M2). RSD values fall under 10% for 200 mg and above portions.

For both methods, but mainly for ICP-MS, the RSD values were higher than the certification confidence interval [19]. Both preparation step and instrumental analysis were implied to explain this variability. For example, the ICP-MS instrumental RSD, obtained by triplicate analyses of a solution, was 2–5%. The INAA instrumental incertitude level is estimated to be between 4 and 5%. These results indicate that (i) the sample preparation prior to ICP-MS is the most scattering step, and (ii) both methods are convenient for biomonitoring surveys, as they do not induce large errors, on an order of magnitude, in the measured concentrations. Increasing the portion weight to 200 mg and above (500 mg are ordinary used for such surveys) would increase the quality of the results.

Detection Limits

The ICP-MS detection limits were calculated as three times the standard deviation over the reagents blank concentrations [18]. Detection limits of ICP-MS depend mainly upon the cleanliness of digestion vessels and on ICP-MS working conditions. Therefore, as the samples were analyzed over a two-year period, the detection limits varied from one batch to another. The INAA detection limits were determined according to the Currie rule [20], with a level of confidence of 97.5%. Element detection limits for INAA are primarily influenced by background gamma activity levels. For example, the presence of relatively large concentrations of a highly activable element introduces high detection limits. In the mosses used in this study, this activity was mainly due to Mn for short irradiation (Al, Cl, Cu, I, Mg, Mn, Ti and V concentration determination can be disturbed), Na for 4-days cooling after long irradiation (As, Au, Br, Cd, K, La, Mo, Na, Sb, Sm and W determination) and Sc for 15-days cooling after long irradiation (Ag, Ba, Ca, Ce, Co, Cr, Cs, Fe, Hg, Rb, Sc, Se, Sr, Th and Zn determination).

INAA and ICP-MS experimental detection limits are provided in Table II. For the ten elements of interest in the European program, the detection limits of each method and the concentration ranges in the French mosses [21] were compared. INAA appeared suitable for the determination of As, Cr, Fe, Hg, V and Zn. ICP-MS sensitivity was well suited for Cd, Cr, Cu, Ni, Pb and V. The As median concentration is close to the ICP-MS detection limits, leading to many results below the limit of detection. INAA and ICP-MS displayed similar sensitivity for Ba, La, Ce, Cs, Eu, Th and W, whereas Co, Sb, Sc and Sm exhibited lower detection limits when analyzed with INAA. Conversely, ICP-MS detection limits were better for Mo, Rb, Sr, Ti and U.

Accuracy

Similarly, the results on inter-calibrated mosses were used to evaluate the accuracy of both methods.

ICP-MS: (Table III) The concentrations of As, Co, Hg, Mo, Ni, Sb, Th, U and W were close to their respective detection limits and, hence, were not precisely determined in M1. However, the other results were in good agreement with the recommended values, with the exception of Co, Cr, Cu, Fe, Sr and V in M2. The higher concentrations of Co, Cr, Fe and Sr could be explained by the use – in our procedure – of hydrofluoric acid during acid digestion. This acid is used for complete mineral dissolution. Fe and V concentrations were in the upper limit of the recommended values (Ar–O and Ar–Cl interference, respectively). Lower Cu contents could be explained by losses during digestion.

INAA: (Table IV) The concentration of the ten elements under investigation in the European program, with the exception of Cd and Cr, were in good agreement with recommended values. For the other elements listed in the French program, discrepancies were observed for Al, Mn, Na, Sr, U and V. Various methods were used to establish the recommended values [19]: ICP-MS, NAA, Atomic Absorption

TABLE II Detection limits (μg g^{-1} dry weight) in French mosses analyzes for ICP-MS and INAA

	INAA	*ICP-MS*
Al	1–5	n.d.
As	0.03–0.05	0.03–0.05
Au	0.0005–0.001	n.d.
Ba	3–14	0.1–5
Bi	n.d.	0.05–0.08
Br	0.03–0.1	n.d.
Ca	50–200	n.d.
Cd	0.2–1.0	0.02–0.1
Ce	0.1–0.4	0.01–0.1
Cl	8–13	n.d.
Co	0.005–0.1	0.01–0.5
Cr	0.1–0.4	0.4–1.1
Cs	0.01–0.06	0.001–0.09
Cu	4–15	0.2–1.7
Eu	0.01–0.05	0.002–0.01
Fe	10–30	10–70
Hg	0.005–0.1	0.03–0.07
I	1–10	n.d.
K	50–100	n.d.
La	0.01–0.07	0.01–0.1
Mg	150–200	n.d.
Mn	1–5	n.d.
Mo	0.2–1	0.01–0.08
Na	5–10	n.d.
Ni	n.d.	0.8–5.0
Pb	n.d	0.1–2
Rb	0.3–2	0.1–0.6
Sb	0.01–0.01	0.02–0.1
Sc	0.001–0.006	3–5
Se	0.1–0.5	n.d.
Sm	0.001–0.006	0.01–0.03
Sr	7–24	0.02–0.2
Th	0.01–0.03	0.01–0.06
Ti	30–70	2–10
U	0.1–1	0.003–0.02
V	0.2–0.8	0.06–0.1
W	0.05–0.1	0.03–0.4
Zn	1.5–3	n.d.
Zr	5–22	n.d.

n.d.: Not determined.

Spectrometry (Flame, Cold Vapor, Graphite Furnace, and Hydride Generation), ICP-Atomic Emission Spectrometry and X-ray Fluorescence Spectrometry. Most laboratories involved in the determination of the reference materials used techniques based on digestion of the sample with strong mineral acids (ICP-MS, ICP-AES and AAS). This procedure can affect the relative concentrations of certain elements (volatility, incomplete digestion, adsorption, colloidal interferences, time evolution of the solution). The laboratories were supposed to use the same digestion process and, as a result, the measurements obtained by the different destructive techniques were in good agreement. In some cases, e.g. Cr, the values produced by INAA, a non-destructive technique, were rejected as outliers because they were too different from the values produced by the destructive techniques. Therefore, the recommended

TABLE III ICP-MS results (in μg/g) obtained for moss standards [19]

	M1			*M2*		
	Mean ± SD	*N*	*Recommended values [19]*	*Mean ± SD*	*N*	*Recommended values [19]*
As	< 1	17	0.070 ± 0.005	0.81 ± 0.19	44	0.98 ± 0.07
Ba	9.8 ± 1.1	17	10.8 ± 0.5	16.3 ± 1.4	28	17.6 ± 0.7
Cd	0.069 ± 0.013	13	0.077 ± 0.006	0.391 ± 0.039	25	0.450 ± 0.019
Ce	0.13 ± 0.04	17	0.15 ± 0.03*[a]	0.31 ± 0.05	44	0.35 ± 0.03*[a]
Co	< 0.2	17	0.124 ± 0.004	1.24 ± 0.28	44	0.98 ± 0.06
Cr	0.55 ± 0.15	17	0.50 ± 0.13[a]	1.18 ± 0.25	44	0.97 ± 0.17[a]
Cs	0.061 ± 0.004	17	0.068 ± 0.009	0.50 ± 0.04	44	0.55 ± 0.04
Cu	2.84 ± 0.34	17	3.18 ± 0.12[a]	62.2 ± 7.1	44	68.7 ± 2.5
Fe	151 ± 71	5	90 ± 12[a]	328 ± 64	17	262 ± 35
Hg	< 0.03	5	0.029 ± 0.002	< 0.03	20	0.058 ± 0.005
La	0.073 ± 0.03214	17	0.071 ± 0.008	0.18 ± 0.03	44	0.195 ± 0.018
Mo	< 0.08	17	0.08 ± 0.04*[a]	0.24 ± 0.06	44	0.23 ± 0.04*[a]
Ni	< 2	17	0.99 ± 0.1	16.0 ± 2.8	44	16.3 ± 0.9
Pb	2.06 ± 0.18	17	2.00 ± 0.13[a]	7.40 ± 0.38	44	6.37 ± 0.43[a]
Rb	18.4 ± 2.0	17	17.6 ± 0.4	41.0 ± 6.2	44	39.6 ± 0.4
Sb	< 0.04	17	0.031 ± 0.006	0.157 ± 0.029	38	0.210 ± 0.016
Sr	3.50 ± 0.51	17	3.45 ± 0.10[a]	5.88 ± 0.88	44	5.31 ± 0.15[a]
Th	< 0.02	17	0.017 ± 0.001	0.049 ± 0.017	44	0.042 ± 0.002
Tl	0.018 ± 0.010	17	0.016 ± 0.002*[a]	0.065 ± 0.013	41	0.048 ± 0.004*[a]
U	0.014 ± 0.006	17	0.0062 ± 0.0013*[a]	0.027 ± 0.008	44	0.021 ± 0.005*[a]
V	0.66 ± 0.08	17	0.60 ± 0.10	1.56 ± 0.24	44	1.43 ± 0.17
W	< 0.05	17	0.045*[a]	0.06 ± 0.02	44	0.089*[a]

SD: Standard deviation; *N*: Number of samples analyzed; *Indicated values; [a]Values obtained by ICP-MS analyses only; [b]Values obtained by INAA analyses only.

values may represent the nitric-acid soluble concentrations of the element. When INAA results were not used to obtain the recommended values – quoted (a)-, our results were sometimes significantly different from the recommended values (e.g. Cr, Na and Sr in M2). When only the INAA results were used for the recommended values – quoted (b)-, the agreement between values is generally quite good (e.g. Br, Cl and Sc). It is worth noting that a good agreement between these present results and the recommended values were observed for some elements at low concentration level (e.g. Hg, W, Th).

Statistical comparison of the results obtained by both methods on naturally growing mosses. INAA and ICP-MS results were compared (see Table V) for 14 elements: As, Ba, Ce, Co, Cr, Cs, Eu, Fe, La, Rb, Sb, Sm, Th and V. Among the 23 elements determined by both methods, 9 elements (Cd, Cu, Hg, Mo, Sc, Sr, Ti, U, W) were not retained when less than 100 pairs could be compared (most of figures under the detection limit for one technique). Satisfying correlation results (R^2 > 60%) appeared for: Ba, Ce, Cs, La, Rb, Sm, Th and V. Among these elements, the slopes were close to unity with a significantly high R^2 for Ba, Cs, La and Sm. A slope significantly less than unity for Ce and Th was calculated. For these two elements either INAA overestimates or ICP-MS underestimates their concentration. ICP-MS may underestimate elemental concentrations if there is incomplete mineral digestion. An INAA overestimate is also possible. For example, Ce is determined through ^{141}Ce, a radioisotope with a 32.5 days half-life that decays with a γ-ray at 145 keV. As a result a possible

TABLE IV INAA results (in μg/g dried weight) obtained for mosses standards [19]

	M1			*M2*		
	Mean ± SD	*N*	*Recommended values [19]*	*Mean ± SD*	*N*	*Recommended values [19]*
Ag	< 0.08	10	0.024 ± 0.006*[a]	0.110 ± 0.014	10	0.137 ± 0.014*[a]
Al	98 ± 4	10	87 ± 7*[a]	243 ± 20	8	178 ± 15[a]
As	0.062 ± 0.004	5	0.070 ± 0.005	0.87 ± 0.04	9	0.98 ± 0.07
Ba	10.8 ± 1.2	10	10.8 ± 0.5	16.1 ± 1.9	10	17.6 ± 0.7
Br	0.99 ± 0.04	10	0.94–1.10[b]	1.03 ± 0.04	10	0.97–1.20[b]
Ca	1536 ± 183	10	1990 ± 50	1670 ± 213	10	1910 ± 100
Cd	< 0.5	10	0.077 ± 0.006	0.834 ± 0.170	10	0.45 ± 0.019
Ce	0.11 ± 0.03	10	0.15 ± 0.03*[a]	0.31 ± 0.09	10	0.35 ± 0.03*[a]
Cl	53 ± 11	9	43–55[b]	105 ± 17	10	105–115[b]
Co	0.107 ± 0.008	10	0.124 ± 0.004	0.95 ± 0.07	10	0.98 ± 0.06
Cr	0.71 ± 0.07	10	0.50 ± 0.13	1.85 ± 0.38	10	0.97 ± 0.17[a]
Cs	0.064 ± 0.006	10	0.068 ± 0.009	0.54 ± 0.07	10	0.55 ± 0.04
Cu	< 11	10	3.18 ± 0.12[a]	63.8 ± 14.0	10	68.7 ± 2.5
Fe	106 ± 14	10	90 ± 12[a]	280 ± 12	10	262 ± 35[a]
Ga	< 0.2	10	0.052 ± 0.013*[a]	< 0.4	10	0.113 ± 0.020*[a]
Hg	0.024 ± 0.010	6	0.029 ± 0.002	0.050 ± 0.009	6	0.058 ± 0.005
K	3530 ± 442	9	3750 ± 290	6677 ± 438	10	6980 ± 350
La	0.072 ± 0.006	10	0.071 ± 0.008	0.181 ± 0.021	10	0.200 ± 0.018
Mg	642 ± 96	10	773 ± 49	705 ± 122	10	826 ± 52
Mn	450 ± 100	10	522 ± 29[a]	256 ± 24	10	342 ± 17
Mo	< 0.3	10	0.08 ± 0.04*[a]	0.51 ± 0.22	8	0.23 ± 0.04*[a]
Na	83 ± 9	10	88 ± 9	215 ± 13	10	166 ± 15[a]
Rb	17.9 ± 0.2	10	17.6 ± 0.4	38.2 ± 1.3	10	39.6 ± 0.4
Sb	0.025 ± 0.004	10	0.031 ± 0.006	0.197 ± 0.032	10	0.210 ± 0.016
Sc	0.020 ± 0.001	10	0.020*[b]	0.052 ± 0.002	10	0.065*[b]
Se	0.098 ± 0.021	9	0.099 ± 0.004[a]	0.32 ± 0.09	10	0.29 ± 0.03
Sm	0.008 ± 0.001	10	0.010–0.012*[b]	0.022 ± 0.002	10	0.030–0.031*[b]
Sr	< 8	10	3.45 ± 0.10[a]	11.70 ± 3.50	8	5.31 ± 0.15[a]
Th	0.016 ± 0.003	10	0.017 ± 0.001	0.036 ± 0.006	10	0.042 ± 0.002
Ti	< 52	10		< 51	10	
U	< 0.07	10	0.0062 ± 0.0013*[a]	0.068 ± 0.025	9	0.021 ± 0.005*[a]
V	0.47 ± 0.09	10	0.60 ± 0.10	1.17 ± 0.20	8	1.43 ± 0.17
W	< 0.06	10	0.039–0.045*[a]	0.063 ± 0.018	5	0.064*[b]
Zn	24.3 ± 1.0	10	25.0 ± 0.9	35.2 ± 1.1	10	36.1 ± 1.2

*Indicated values; [a]No INAA results used for the certification; [b]Indicated values obtained by INAA analyses only.

interference from ^{59}Fe (γ-emission 142.5 keV) can occur. This is particularly the case for mosses as Fe concentrations are often high. In addition, a spectral interference of an escape peak, due to ^{60}Co, on the 311.8 keV peak of ^{233}Pa, which is used to determine Th, can explain the INAA overestimation of this element. Poorer linear correlation results were obtained for As, Eu, Fe and Sb. The concentrations measured by ICP-MS for As and Eu were generally higher than those measured by INAA. This would be a result of the interference of ^{40}Ar^{35}Cl for As and ^{135}Ba^{16}O/^{134}Ba^{16}O^{1}H for Eu. Interference of sulfur-complexes with As determinations is also possible. Problems related to the digestion process (incomplete digestion for Fe and volatile losses for Sb) may explain higher concentrations measured with INAA.

No significant correlation is obtained for Co and Cr. Cobalt determinations using ICP-MS may be masked through the recombination between Ca and O (e.g. ^{43}Ca^{16}O). In the particular case of Cr, the INAA results were generally twice

TABLE V Statistical comparison of INAA and ICP-MS data. Student t-tests for paired data with significance level 95%, $p < 0.05$,*$p < 0.01$, **$p < 0.001$. R^2: determination coefficient for linear correlation

Elements	*Number of tested pairs*	*INAA* (μg g^{-1}) *(calculated for tested pairs)*		*t-Test results*	*ICP-MS* (μg g^{-1}) *(calculated for tested pairs)*		*Slope*	*Intercept*	R^2 (%)
		Mean	*Variance*		*Mean*	*Variance*			
As	408	0.50	0.41	< **	0.63	0.39	0.67	0.30	48
Ba	540	31.1	383	=	31.9	648	1.11	−2.51	72
Ce	543	1.95	4.62	> **	1.66	2.76	0.69	0.33	79
Co	561	0.48	0.13	< **	1.35	9.22			
Cr	563	4.14	13.13	> **	2.18	3.71			
Cs	551	0.41	0.87	< **	0.43	0.71	0.87	0.08	93
Eu	212	0.026	0.001	< **	0.038	0.001	0.76	0.02	49
Fe	267	711	626	> *	656	689	0.79	93	51
La	530	1.90	12.62	> **	1.76	12.68	0.96	−0.07	92
Rb	572	17.7	220.4	< **	19.0	308.8	0.96	1.99	66
Sb	167	0.21	0.02	> **	0.15	0.02	0.70	0.003	55
Sm	213	0.18	0.07	=	0.19	0.08	0.99	0.01	86
Th	475	0.26	0.10	> **	0.23	0.05	0.65	0.06	77
V	572	3.10	4.22	< **	3.62	5.52	0.92	0.75	65

higher than the ICP-MS results. No correlation was observed between ICP-MS and INAA results for Cr. Six hypotheses have been formulated to explain this discrepancy:

(i) *Contamination by the cellulose powder used to prepare the pellets (INAA):* The cellulose was analyzed by INAA and the chromium contamination corresponded to 0.08 ± 0.03 μg g^{-1} dry-weight of the moss.

(ii) *Contamination occurring when preparing the pellet (INAA):* Pellets of cellulose were then analyzed (INAA) and the chromium contamination corresponded to 0.19 ± 0.01 μg g^{-1} dry-weight of the moss. However, this real contamination is not high enough to explain the discrepancy between both methods. In the case of the French mosses, ICP-MS and INAA results were, on average, 2.2 and 4.1 μg g^{-1}, respectively.

(iii) *Overestimation by INAA:* A primary standard of chromium (Al wire doped with 0.105% Cr) was analyzed by INAA. The measured concentration (0.107 ± 0.002%) proved no systematic overestimation by INAA.

(iv) *Interferences with INAA:* Chromium is measured through its radioisotope ^{51}Cr, (half-life: 27 days, γ-energy: 320 keV). The only other radioisotopes having a γ-ray with similar energy (± 1 keV) are ^{51}Ti, ^{147}Nd and ^{177}Lu. The half-life of ^{51}Ti is 6.6 min – too short to be observed after a decay time greater than 7 days. ^{147}Nd and ^{177}Lu have long half-life times (11 and 6.7 days, respectively), but both radioisotopes have more intense energy peaks which were not observed in the spectra. A possible nuclear interference from the reaction ^{54}Fe(n,α)^{51}Cr must also be considered. The Orphée reactor used in these experiments provides a high thermal neutron flux but also a very weak fast neutron flux which is responsible for threshold reactions like (n,α) reactions. The interference due to the ^{54}Fe(n,α)^{51}Cr reaction can be calculated as low as 10^{-8} g of Cr per g of Fe, which is extremely negligible, given the amount of Fe in mosses.

(v) *Underestimation using ICP-MS:* An intercomparison with Atomic Absorption Spectrometry (AAS) revealed that no discrepancy occurred between ICP-MS and AAS measurements when identical digestion solutions were analyzed [22].

(vi) *Incomplete digestion or volatilization during digestion (ICP-MS):* These results tended to prove that the digestion step prior to ICP-MS is responsible for the discrepancy. Nevertheless, the same digestion process was applied successfully to lichen [14], suggesting that the discrepancy may be matrix-dependent.

European maps were published on 1998 [2]. In these colored contour maps, the concentrations are ranged in classes, from low (green) to high concentrations (red). For mapping the French results (all results are not available), we chose INAA results for As, Cr, Fe, V and Zn, and ICP-MS results for Cd, Cu, Ni and Pb. The consequences on the interpretation of the maps are evaluated with comparison to generate with the results provided by other analytical methods. This choice leads to a slight "underestimate" of As concentrations and a large "overestimate" of Cr concentrations. Due to the range of concentrations chosen to draw the European maps, the "ICP-MS" map for Cr would be more green than the "INAA" map. Conversely, the "INAA" map for As is more green than the "ICP-MS" map. For V, no change is observed between the two maps, because the discrepancy does not imply color class change. For Cu, the use of INAA leads to numerous figures under detection limits, which are not usable for mapping.

CONCLUSION

The use of INAA and ICP-MS extends the number of elements that can be determined by using a single technique. Only ICP-MS allows the measurement of Pb. ICP-MS improves Cd, Cu and Ni determinations. On the other hand, only INAA allows the determination of Br, Cl, K and Mn. When results were obtained by both methods, for a total of 23 elements (among them: As, Co, Cr, Fe), the choice is determined on the most convenient method. To build the French database of trace element concentrations in mosses, ICP-MS results were used for Cd, Cu, Ni, Pb. INAA was chosen, due to its better accuracy, for the determination of the other elements. This work shows that the combination of analytical techniques having very different principles to draw contour maps may sometimes lead to erroneous interpretations. These maps have to be studied bearing in mind the analytical processes used to produce the data. For spatio-temporal trends, the analytical procedure has to be precisely described prior to the analyses to ensure further data comparison. In the case of Cr, it proves that the ICP-MS results do not represent the total content of the moss. If ICP-MS is retained as the routine method, the digestion step must be strictly the same for all samples. In remote areas, most of the particle burdens in mosses are soil dust. The control of mineral dissolution is, thus, of great importance.

Another important aspect involves the methods used to calibrate reference materials. ICP-MS, ICP-OES and AAS are now, and probably will be in the future, the most employed analytical techniques for trace element determination. This biases results towards these wet-chemistry analytical methods. As all of the wet-chemical techniques should provide a similar result for the same solution – the results can be accepted. However, when these techniques are applied to define elemental concentrations in reference materials, the "recommended value" is biased by the chemical treatment (volatile losses, incomplete dissolution, adsorption or any other process occurring in solutions at very low concentrations). Consequently, reference materials must be inter-calibrated assuming a reasonable balance between destructive and nondestructive analytical methods.

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References

[1] A. Rühling and G. Tyler. *Bot. Notiser*, **121**, 321–342 (1968).
[2] A. Rühling and E. Steinnes. *Nord*, **15**, 66pp (1998).
[3] L. Galsomiès, M.A. Letrouit-Galinou, C. Deschamps, D. Savanne and M. Avnaim. *Sci. Total Environ.*, **232**, 39–47 (1999).
[4] G. Tyler. *Bot. J. Linn. Soc.*, **104**, 231–253 (1990).
[5] R. Herrmann. In: H.D. Zinsmeister and R. Mues (Eds.), *Bryophytes Their Chemistry and Chemical Taxonomy*, pp. 319–335, Oxford Science Publication, Oxford (1990).
[6] J.H. Halleraker, C. Reimann, P. de Caritat, T.E. Finne, G. Kashulina, H. Niskaavaara and I. Bogatyrev. *Sci. Total Environ.*, **218**, 123–139 (1998).
[7] B. Markert. In: B. Markert (Ed.), *Plants as Biomonitors: Indicators for Heavy Metals in the Terrestrial Environment*, 643pp, VCH, Weinheim (1993).
[8] M.H. Martin and P.J. Coughtrey. *Biological Monitoring of Heavy Metal Pollution*, 475pp, Applied Science Publishers, London (1982).
[9] R. Bargagli. *Trace Elements in Terrestrial Plants*, pp. 207–236, Springer, Berlin (1998).
[10] E. Steinnes, J.E. Hanssen, J.P. Rambaek and N.B. Vogt. *Water, Air, and Soil Pollution*, **74**, 121–140 (1994).
[11] B. Markert and V. Weckert. *Toxicol. Environ. Chem.*, **40**, 43–56 (1993).
[12] B. Markert. In: B. Markert (Ed.), *Instrumental Analysis of Plants*, pp. 111–176, VCH, Weinheim (1996).
[13] E. Steinnes, O. Johansen, O. Royset and M. Odegard. *Environ. Mon. Asses.*, **25**, 87–97 (1993).
[14] G. Revel and S. Ayrault. *J. Radioanal. Nucl. Chem.*, **244**, 73–80 (2000).
[15] A. Senhou, A. Chouak, R. Cherkaoui, M. Lferde, A. Elyahyaoui and T. El Khoukhi *et al. J. Radioanal. Nucl. Chem.*, **253**, 247–252 (2002).
[16] L. Galsomiès, M.A. Letrouit-Galinou, C. Deschamps, D. Savanne, M. Avnaim and G. Duclaux. *Proc. Int. Conf. Biomonitoring on Atmospheric Deposition*, Lisboa, 21–24 Sept. 1997, *IAEA Tecdoc*, Vol. 1152, pp. 108–115 (2000).
[17] D. Piccot, C. Deschamps, R. Delmas and G. Revel. *J. Radioanal. Nucl. Chem.*, **215**, 263–269 (1997).
[18] S. Ayrault, P. Bonhomme, F. Carrot, G. Amblard, M.D. Sciarretta and L. Galsomiès. *Biol. Trace Elem. Res.*, **79**, 177–184 (2001).
[19] E. Steinnes, A. Rühling, H. Lippo and A. Mäkinen. *Accred. Qual. Assur.*, **2**, 243–249 (1997).
[20] L.A. Currie. *Anal. Chem.*, **40**, 587–593 (1968).
[21] L. Galsomies, D. Savanne, M.A. Letrouit, S. Ayrault and B. Charre. In: ADEME (Ed.), *Retombées atmosphériques de métaux en France: estimation par dosage dans des mousses*, pp. 31, ADEME, Paris (1999).
[22] M. Dapiaggi, F. Leva, D. Rabuffetti, S. Ayrault, A. Gaudry and R.M. Cenci. *Environ. Technol.*, **22**, 1183–1192 (2001).