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Multi-element ICPMS analysis of moss used as biomonitor of air pollutants

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Summary

ICPMS was used to study the elemental composition of 550 moss samples used for biomonitoring of atmospheric deposition. Elements investigated were Li, Be, B, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Mo, Cd, Sb, Te, Cs, Ba, La, Hg, Tl, Pb, Bi, Th and U. Of the 30 elements studied, 24 were present above detection limits in more than 99% of the samples. The precision was typically 10% or better for 15 of the elements and 10-20% for another 11 elements. About one third of the elements were determined routinely with an accuracy of 10% or better, as evident from the analysis of standard reference materials, while another one third was determined to an accuracy of 10-20%. On the basis of this work, ICPMS was judged equivalent to a previous scheme for this purpose based on a combination of INAA and AAS.

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1. Introduction

Mosses are useful as biomonitors of atmospheric deposition of trace elements, including most of the heavy metals of primary concern in environmental pollution studies. In the Nordic countries moss surveys of heavy metal deposition comprising about 2000 sites are being carried out every 5 years[1]. Each country is responsible for its own analyses, and the techniques employed vary a great deal. As a minimum, they must allow sensitive and accurate determination of the 9 elements V, Cr, Fe, Ni, Cr, Zn, As, Cd and Pb, but additional information is desirable.

In the Norwegian part of this survey a combination of instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS) has been employed[2] , allowing the determination of nearly 30 elements in moss samples. In connection with an inter comparison exercise carried out between all Nordic laboratories that were potential participants in the 1990 moss survey, it was decided to compare the performance of the hitherto used INAA/AAS scheme with other multi-element approaches. As a result of this test[3], ICPMS was assumed to yield satisfactory data for the 9 elements of priority and also for most other elements previously studied in Norwegian moss surveys. In addition, there was a potential for obtaining data on elements such as Ga, Te, Tl and Bi for which very little information existed so far about their possible role in air pollution. It was therefore decided to use ICPMS as the main analytical technique in the Norwegian part of the 1990 Nordic heavy metal deposition survey. In addition, about one third of the samples were also subjected to INAA.

In this paper the performance of ICPMS for multi-element analyses of moss samples used as biomonitor of atmospheric deposition of trace elements is discussed on the basis of experience from the 1990 survey.

2. Experimental

2.1 Samples

The Nordic moss surveys are based on either Hylocomium splendens or Pleurozium schreberi, both mosses growing on the ground and shown to have very similar properties with regard to the uptake of trace metals from the atmosphere. In the Norwegian part of the survey practically all samples were Hylocomium splendens. Procedures for field collection of samples are given elsewhere[1]. After drying the moss samples at 30°C and removal of extraneous material, the upper three segments of each plant were taken for analysis. Previous experience had shown that samples prepared in this way are sufficiently homogeneous for analysis with the sample sizes used in this work[3,4].

2.2 ICPMS

The elemental analysis were performed with a Plasmaquad I instrument (VG-Elemental, UK) equipped with a Meinhard nebulizer, water cooled spray chamber, VG-type torch, Ni sample and skimmer cones and electron multiplier detector in pulse counting mode. The data acquisition was performed in scan mode from 6 - 244 amu with the isotopes shown in Table 1. The isotope 57 was used for Fe, while mass 60 was used for Ni as the mass 60 is less affected by overlap from Fe and CaO than mass 58. Standards were prepared from high purity element standards (Spectrascan, Teknolab A/S, Norway). Working standard solutions of 50 and 250 ng ml^{-1} were used for the trace elements, while additional standards of 1000 ng ml^{-1} were used for the major elements (Na, Mg, Al, Ca, Mn and Fe). All standards were matched with the nitric acid concentration of the samples. Three internal standards (Sc, In and Re) at a concentration of 50 ng ml^{-1} were used. The samples (0.50 g dry matter) were digested with 8 ml of conc. nitric acid (Merck supra pure) in closed PTFE-bombs at 160 ^{o}C for 6-8 hours, cooled and diluted to a volume of 50 ml by demineralized water.

2.3 Blank control and detection limits

Due to the high sensitivity of ICPMS the practical detection limits obtained are limited by the blank values of the sample pretreatment procedure. This is generally the case using PTFE-bombs for digestion of biological material. Although very convenient for the digestion of plant material, closed PTFE-bombs are subject to cross contamination from preceding samples digested in the same bomb. To keep the blank values as low as practically possible, the following rinsing procedure has proved to be useful: Before use the bombs were filled with 20 % nitric acid, closed and heated (160 ^{o}C) and cooled in cycles of 4 hours in a laboratory oven for at least a week. The blank values of the rinsed bombs were then determined by performing a digestion with only nitric acid, and only bombs with acceptable low blank values were used. During use a blank digestion were performed for every sixth bomb, in order to keep track with the blank values. A full rinsing procedure of the bombs was performed if the blank values were found to increase. All the results for the blank values were collected, and the mean and standard deviation were calculated. The practical detection limit was defined as three times the standard deviation. The mean value for the blank is subtracted from the result for each element, the remainder is compared to the obtained detection limit and accepted if above. If less, the results are expressed as below the detection limit. The practical detection limits obtained for the determination of elements in plant material using this digestion procedure are shown in Table 1.

2.4 INAA

Weighed samples of about 0.3 g were wrapped in aluminum foil and irradiated for 20 h in the JEEP-II reactor (Kjeller, Norway) at a thermal neutron flux of about $1.2x10^{13}$ n cm^{-2} s^{-1} along with appropriate standards. After 3-4 days' delay the samples were transferred to inactive counting vials and assayed by gamma-spectrometry using a germanium detector (1.7 keV FWHM, 12.5% relative efficiency, both at 1332 keV). As and Sb were determined on the basis of measurements performed 4-5 days after the end of the irradiation, while an additional measurement

after 3-4 weeks facilitated the determination of Cr, Fe, Co, Zn and Se. Details on the INAA procedure are reported elsewhere[2].

2.5 Reference materials used

The standard reference materials from the U.S. National Institute of Standards and Technology (NIST) SRM-1572 (Citrus Leaves), SRM-1575 (Pine Needles) and SRM-1577a (Bovine Liver) were run between every 50 samples during the analysis of the 550 moss samples. In addition replicates of a moss reference sample (NORD-DK2) prepared for the inter comparison exercise preceding the 1990 Nordic moss survey, the identity of which was not known to the analytical laboratory, was run in random order in-between the ordinary samples.

3. Results and discussion

3.1 Precision of ICPMS

The moss reference sample NORD-DK2 has a composition not differing greatly from the mean composition of the 550 samples. The results (Table 1) from the replicate analyses of this reference moss indicate the average precision obtained by ICPMS analysis of moss samples used as biomonitors. The figures are as follows:

<5%	V, Fe, Zn, Rb, Sr, Ba, Pb
5-10%	B, Al, Mn, Cu, Y, Cs, La, Tl
10-20%	Li, Cr, Co, Ni, Ga, As, Mo, Cd, Sb, Bi, V
>20%	Be, Te, Hg, Th

Thus, a precision of 10% or better is evident for 15 elements, while another 11 elements showed a precision between 10-20%.

Figure 1 show further details of how the precision varies with concentration. At concentrations above 1 µg g-1 dry matter the precision is mostly below 10 %. When the concentration moves downward towards the detection limits around 0.001 - 0.01 µg g-1, the precision increases gradually to about 50 %.

3.2 Sensitivity and detection limits for ICPMS

The results in Table 1 shows that detection limits from 1 - 10 µg g^{-1} were obtained for the major elements, while figures from 0.001 - 0.1 µg g^{-1} were obtained for most of the trace elements. The ranges for the 30 elements monitored in the moss samples (Table 1), shows that 22 elements were present above detection limits in all samples, 4 elements (As, Mo, Sb, Th) were below the detection limit in less than 1%, 3 elements (Cr, Cd, La) in about 10%, 1 element (Hg) in about 30%, and 2 elements (Be, Te) in more than 50% of the samples. Parts of the results for Na, Mg and Ca are above the linear range for ICPMS, and dilution would be necessary for accurate measurements.

Figure 2a shows graphically the detection limits obtained, together with the minimum and median values for the Norwegian moss sample data set. Obviously, the median values are at least a factor of ten higher than the practical detection

limits for most elements except for Te, Cd, Hg, Cr and Ni. It also show that the blank values from the digestion systems are highest for the major elements. For the least abundant elements the blank values are also the least problematic. The detection limits for the trace elements may be kept in the order of 1000 times lower than for the major elements. This is most probably due to the problems with cleaning of the Teflon bombs in between different samples. As Teflon is a fairly porous material, it may be difficult to rinse the contamination located in small pores in the inner wall of the vessel. This cross contamination effect is thus much more predominant for the major than for the trace elements.

Figure 2b shows the relation between the detection limits obtained by the blank values from the bombs and the practical detection limit obtained by ICPMS. For most elements the blank values obtained from the bombs are 10 - 100 times higher than the practical detection limit for the ICPMS-technique alone. To improve the detection power for the Teflon bomb digestion/ICPMS-analysis system the blanks values originating from the Teflon bombs must be reduced.. Recent experience with more thorough cleaning procedures for the bombs in between each digestion have shown that it may be possible to reduce the blanks from the bombs.

3.3 Accuracy

The accuracy of the analyses can to a great extent be judged on the basis of data obtained for reference materials (Table 2-6 and Figure 3) and the comparisons with INAA (Figure 3/Table 6). On average, 16 of 30 elements studied in this work are certified in the NIST SRM's. SRM 1572 Citrus Leaves and 1575 Pine needles are the two NIST samples most closely matching moss in elemental composition. The agreement obtained for these materials is as follows: <5%, 4 elements; 5-10%, 4 elements; 10-20%, 3 elements; and >20%, 4 elements. For the moss reference sample NORD-DK2 the figures are somewhat better: 6, 8, 1 and 1 elements respectively. SRM 1577 Bovine liver has an element composition not simulating the moss samples very well, but the data are reported here to show the good performance of ICPMS for elements such as Sr and Pb even if present at levels far below those normally encountered in mosses.

Among the elements included in this study, no certified values existed in the NIST reference materials for 9 elements, i.e. Li, Be, B, Ga, Y, Te, La, Tl and Bi, so that no conclusions can be drawn about the accuracy of the ICPMS determinations. For some of the other elements, specific comments pertaining to the accuracy of the results are given below.

3.4 Comparison between ICPMS and INAA

Figure 4 and Table 6 show the results obtained for Cr, Fe, Co, Zn, As and Sb determined by both ICPMS and INAA. The results for Cr express to a certain extent the effect of incomplete dissolution; the ICPMS data appear to be systematic low. The results for Fe, Co and As are reasonably similar with both techniques (linear regression slopes between 0.93 and 1.06). Some low results obtained by ICPMS for Fe and Co may be explained by low digestion efficiency. The results for Sb are also

systematic low by ICPMS compared to INAA; the reason for which is presently not clear.

3.5 Effect of digestion efficiency

Previous experience from deposition surveys employing moss samples shows that processes other than air pollution contribute significantly to the elemental composition of the mosses[5]. Principal component analysis identified a prominent compound apparently associated with soil particulates of local origin, presumably supplied as windblown dust. Among the elements of interest is the present paper, this principal component showed high loadings for Na, Al, Cr, Fe and Th. The nitric acid decomposition used in this work probably dissolves most of the elements in the moss samples associated with air pollution, while it certainly does not break down all mineral matter included in the soil dust. For elements with a significant fraction contained in this mineral matter, the ICPMS results based on acid decomposition may therefore be significantly lower than those from INAA, reflecting the total content in the moss.

3.6 Primary priority elements (V, Cr, Fe, Co, Ni, Cu, Zn, As, Cd and Pb)

An accuracy for V of 10 % or better at levels above 3 $\mu g\ g^{-1}$ is indicated from the analysis of NORD-DK2. Reference values do not exist at lower levels. From the analysis of reference materials an accuracy of 10% is indicated for Cr at the 1 $\mu g\ g^{-1}$ level. Poor agreement is observed with INAA for moss samples (Fig. 4) presumably because of insufficient digestion as discussed above. The results for Fe, Co and Ni in SRM 1572 Citrus Leaves shows clearly the positive interference from the CaO/CaOH-molecular ions at masses from 56 to 60 amu as the Ca-content of 31500 $\mu g\ g^{-1}$ is 2 - 5 orders of magnitude higher than those for Fe, Co and Ni. Reasonably good agreements for Fe observed in samples with lower Ca-content (SRM 1575 and NORD DK2) even though the sensitivity of the ^{57}Fe isotope is low, and lower accuracy might be expected. For those materials where reference values exist for Co, the present mean values agree within 15%. INAA and ICPMS values (Fig. 4) are generally in agreement within 20%. The Ni content in the NIST SRM's is close to the detection limit of the present ICPMS procedure, but the results on NORD-DK2 indicate an accuracy of 10 - 20 % at levels exceeding 2 $\mu g\ g^{-1}$.

The data for reference materials indicate an accuracy of 10% or better for Cu and Zn within the concentration range encountered in mosses (20 - 60 $\mu g\ g^{-1}$ where most of the moss samples fit in). The results for Cu and Zn are somewhat low for SRM 1577a Bovine Liver probably due to that the upper linear range for ICPMS may be exceeded.

ICPMS seems to be satisfactory for determining As in mosses, as an accuracy better than 10% for As at the 3 $\mu g\ g^{-1}$ level and 20% at the 0.2-0.5 $\mu g\ g^{-1}$ level are obtained for the SRM's. The agreement with INAA (Fig. 4) is not entirely satisfactory, however, but still it seems that ICPMS is capable of disclosing reasonably well regional differences in As deposition as reflected by mosses. Satisfactory accuracy for Cd (10-20%) seem evident at levels above 0.2 $\mu g\ g^{-1}$ Cd. The results for SRM 1572 Citrus Leaves indicates that the deviation between measured and certified values are of the same magnitude at levels approaching the detection limit (0.03 $\mu g\ g^{-1}$ in moss)

as those at 0.4 µg Cd g^{-1} (SRM 1577a Bovine liver). The accuracy for Pb seems to be better than 10% in the entire concentration range observed in the 1990 mosses (1.5 - 80 µg g^{-1}), as good agreement is encountered for all the reference materials.

3.7 Other elements

About 20% low values for Al in SRM 1572 and SRM 1575 might possibly be associated with low digestion efficiencies of mineral matter in these samples. For NORD-DK2 the present value is in agreement with the reference value. The accuracy of Mn determination is generally better than 10%. An exception is observed for SRM 1575 Pine Needles where the present value is 15% lower than the certified one. For Mo a precision of the order of 20% is apparent at the 0.1 µg g^{-1} level, but the results for SRM 1577a Bovine Liver indicate a significantly better precision and accuracy above 1 µg g^{-1}. Both the comparison with INAA and data for reference samples indicate that the Sb data by ICPMS are slightly low, but they appear to be consistent.

In all reference samples Te concentration levels appear to be below the detection limit (0.03 µg g^{-1}). In the moss samples from the 1990 national survey Te was above the detection limit in <20% of the samples. The few samples where it did show appreciable levels were from places with a generally elevated air pollutant level either from local sources or long range atmospheric transport. The precision for Hg at the level of interest in mosses (around 0.1 µg g^{-1}) is rather poor, but data on SRM's indicate that the values observed are still of sufficient quality for order of magnitude judgements.

4. Conclusion

ICPMS as applied in this work seems to provide useful information for all the 30 elements studied in moss samples, either about atmospheric deposition or about contribution to the moss from other sources such as soil dust and leaching from higher plants[4]. It appears to give satisfactory results for the 9 priority elements in the Nordic heavy metal deposition survey[1], and has shown to be a valid alternative to the combination of INAA and AAS used in previous surveys[2]. In addition to these elements, several other trace elements could be determined by ICPMS, such as the elements Be, Ga, Te, Tl and Bi, for which very little is known so far with regard to their occurrence and behaviour as pollutants.

5. References

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Table 1: Summary of ICPMS analysis conditions (isotope masses of the elements), blank values and practical detection limits, compared to the gross composition of the moss samples in the 1990 moss survey.

Element	Summary of ICPMS analysis conditions				Summary of 1990 moss survey		
	Mass	Blank values, a)		Detection	Minimum	Maximum	Median
		Mean	St. dev.	limit, a)	value	value	value
	amu	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}	µg g^{-1}
Li	7	0.002	0.002	0.006	0.03	6.33	0.23
Be	9	0.005	0.007	0.021	<0.021	0.34	0.021
B	11	0.05	0.048	0.15	0.46	47.1	3.1
Na	23	0.6	1.8	5.4	25	870	121
Mg	25	1.4	1.4	4.2	470	4620	1204
Al	27	1.5	1.35	4.05	115	6040	432
Ca	44	2.2	1.4	4.2	1330	12200	-
V	51	0.004	0.006	0.018	0.63	35.0	2.38
Cr	53	0.09	0.16	0.48	<0.48	29.9	0.91
Mn	55	0.017	0.022	0.066	32.0	3150	295
Fe	57	1.1	1.7	5.1	129	18200	472
Co	59	0.003	0.004	0.012	0.055	13.7	0.25
Ni	60	0.15	0.17	0.51	0.50	318	1.56
Cu	65	0.032	0.046	0.138	2.1	42	5.2
Zn	66	0.27	0.33	0.99	8.9	576	36.1
Ga	69	0.006	0.004	0.012	0.024	20.1	0.20
As	75	0.013	0.01	0.03	<0.03	3.23	0.27
Rb	85	0.005	0.004	0.012	1.08	61.9	10.5
Sr	88	0.003	0.005	0.015	2.73	145.0	13.5
Y	89	0.001	0.001	0.003	0.049	2.44	2.22
Mo	95	0.003	0.004	0.012	<0.012	1.20	0.15
Cd	111	0.015	0.011	0.033	<0.033	3.37	0.13
Sb	121	0.003	0.002	0.006	<0.006	0.637	0.09
Te	128	0.015	0.011	0.033	<0.033	0.23	<0.033
Cs	133	0.003	0.007	0.021	0.02	2.51	0.18
Ba	138	0.012	0.015	0.045	4.47	107.6	23.7
La	139	0.011	0.007	0.021	<0.021	6.8	0.44
Hg	201	0.018	0.019	0.057	<0.057	0.88	0.06
Tl	203	0.001	0.001	0.003	0.0059	0.681	0.06
Pb	208	0.010	0.011	0.033	1.52	78.9	9.2
Bi	209	0.0008	0.0007	0.0021	0.002	0.909	0.03
Th	232	0.0008	0.0009	0.0027	<0.0027	1.78	0.08
U	238	0.0004	0.0004	0.0012	0.004	2.30	0.04

a) The mean, standard deviation and detection limits are calculated from the data obtained from the blank control (76 samples) of the PTFE-bombs (see experimental for details). The data are expressed in units of µg g^{-1} of dry matter for 500 mg sample digested with 8 ml nitric acid, diluted to a final volume of 50 ml.

Table 2: ICPMS data for NIST standard reference materials analysed together with the moss samples (results in µg g^{-1} dry matter).

Element	NIST SRM 1572 Citrus Leaves					
	ICPMS			Certified		ICPMS / Cert.
	Mean	S. d.	CV %	Mean	S.d.	% a)
Li	0.208	0.021	10.1			
Be	<0.02	<0.02				
B	60	3	5.0			
Na	152	5	3.3	160	20	-5.0
Mg	4860	470	9.7	5800	300	-16.2
Al	69	5	7.2	92	15	-25.0
Ca	28400	1500	5.3	31500	2000	-9.8
V	0.22	0.02	9.1			
Cr	0.88	0.06	6.8	0.8	0.2	10.0
Mn	21.8	1.5	6.9	23	2	-5.2
Fe	234	60	25.6	90		160.0
Co	0.065	0.017	26.2	<0.02		
Ni	1.1	0.3	27.3	0.6	0.3	83.3
Cu	16.9	1.7	10.1	16.5	1	2.4
Zn	28.2	2.1	7.4	29	2	-2.8
Ga	0.032	0.012	37.5			
As	3.07	0.18	5.9	3.1	0.3	-1.0
Rb	4.79	0.25	5.2	4.84	0.06	-1.0
Sr	92.2	2.9	3.1	100	2	-7.8
Y	0.29	0.02	6.9			
Mo	0.11	0.02	18.2	0.17	0.09	-35.3
Cd	0.05	0.02	40.0	0.03	0.01	66.7
Sb	0.03	0.01	33.3	<0.04		
Te	<0.03	<0.03		<0.02		
Cs	0.1	0.008	8.0	<0.09		
Ba	19.6	1.1	5.6	21	3	-6.7
La	<0.2			<0.19		
Hg	0.11	0.05	45.5	0.08	0.02	37.5
Tl	0.006	0.003	50.0	<0.01		
Pb	12.3	0.5	4.1	13.3	2.4	-7.5
Bi	0.022	0.003	13.6			
Th	0.014	0.004	28.6			
U	0.029	0.006	20.7	<0.15		

a) The ICPMS/certified-value expresses the deviation in % between the results obtained by ICPMS and the certified value.

Table 3: ICPMS data for NIST standard reference materials analysed together with the moss samples (results in µg g^{-1} dry matter).

Element	NIST SRM 1572 Citrus Leaves					
	ICPMS			Certified		ICPMS / Cert.
	Mean	S. d.	CV %	Mean	S.d.	% a)
Li	0.17	0.026	15.3			
Be	0.04	0.02	50.0			
B	15.6	1.5	9.6			
Na	14.1	1.5	10.6			
Mg	1070	80	7.5			
Al	447	41	9.2	545	30	-18.0
Ca	4230	110	2.6	4100	200	3.2
V	0.32	0.03	9.4			
Cr	2.27	0.09	4.0	2.6	0.2	-12.7
Mn	572	43	7.5	675	15	-15.3
Fe	183	8	4.4	200		-8.5
Co	0.1	0.018	18.0	<0.1		
Ni	2	0.2	10.0	<3.5		
Cu	2.6	0.3	11.5	3	0.3	-13.3
Zn	56.3	2.3	4.1			
Ga	0.085	0.012	14.1			
As	0.23	0.04	17.4	0.21	0.04	9.5
Rb	11.3	0.4	3.5	11.7	0.1	-3.4
Sr	4.22	0.22	5.2	4.8	0.2	-12.1
Y	0.08	0.01	12.5			
Mo	0.13	0.02	15.4			
Cd	0.15	0.05	33.3	(<0.05)		
Sb	0.172	0.015	8.7	<0.2		
Te	<0.03	<0.03				
Cs	0.117	0.01	8.6			
Ba	6.4	0.3	4.7			
La	<0.2	<0.2		<0.2		
Hg	0.14	0.07	50.0	0.15	0.05	-6.7
Tl	0.042	0.005	11.9	<0.05		
Pb	10	0.4	4.0	10.8	0.5	-7.4
Bi	0.016	0.009	56.3			
Th	0.025	0.005	20.0	0.037	0.003	-32.4
U	0.0119	0.0013	10.9	0.02	0.004	-40.5

a) The ICPMS/certified-value expresses the deviation in % between the results obtained by ICPMS and the certified value.

Table 4: ICPMS data for NIST standard reference materials analysed together with the moss samples (results in µg g^{-1} dry matter).

Element	NIST 1577a Bovine Liver					
	ICPMS			Certified		ICPMS Cert. % a)
	Mean	S. d.	CV %	Mean	S.d.	
Li	0.188	0.014	7.5			
Be	<0.02					
B	0.63	0.14	22.2			
Na	1500	40	2.7	2430	130	-38.3
Mg	518	23	4.4	600	15	-13.7
Al	<4.0			<2		
Ca	188	20	10.6	120	7	56.7
V	0.14	0.07	50.0	0.099	0.008	41.4
Cr	<0.5					
Mn	9.7	0.6	6.2	9.9	0.8	-2.0
Fe	164	9	5.5	194	20	-15.5
Co	0.201	0.016	8.0	0.21	0.05	-4.3
Ni	<0.5			-		
Cu	135	7	5.2	158	7	-14.6
Zn	110	6	5.5	123	8	-10.6
Ga	0.02	0.01	50.0			
As	0.09	0.07	77.8	0.047	0.006	91.5
Rb	11.9	0.7	5.9	12.5	0.1	-4.8
Sr	0.138	0.008	5.8	0.138	0.003	0.0
Y	<0.003					
Mo	3.62	0.16	4.4	3.5	0.5	3.4
Cd	0.42	0.1	23.8	0.44	0.06	-4.5
Sb	<0.007			0.003		
Te	<0.03					
Cs	<0.02					
Ba	0.07	0.014	20.0			
La	<0.2					
Hg	<0.05			0.004	0.002	
Tl	<0.002			0.003		
Pb	0.112	0.008	7.1	0.135	0.015	-17.0
Bi	<0.002					
Th	<0.003					
U	<0.001			0.00071	0.00003	

a) The ICPMS/certified-value expresses the deviation in % between the results obtained by ICPMS and the certified value.

Table 5: ICPMS data for the moss reference sample NORD-DK2 analysed together with the moss samples (results in μg g^{-1} dry matter).

Element	NORD DK2					
	ICPMS			Intercali-bration 1989	Refer-rence value	ICPMS Ref. value
	Mean	S. d.	CV %	Mean	Mean	% a)
Li	0.40	0.06	15.0	0.28	-	
Be	0.03	0.01	33.3	0.02	-	
B	4.40	0.4	9.1	3.1	-	
Na	240	29	12.1	197	205	17.1
Mg	880	60	6.8	765	800	10.0
Al	588.	47	8.0	455	560	4.8
Ca	2680	140	5.2	1800	1900	41
V	3.55	0.16	4.5	3.19	3.3	7.0
Cr	1.36	0.15	11.0	1.08	1.4	-2.9
Mn	559	39	6.9	820	610	-9.1
Fe	603	24	4.0	580	600	0.5
Co	0.26	0.04	15.4	0.23	0.29	-11.5
Ni	1.86	0.22	11.8	1.6	2	-7.5
Cu	5.90	0.5	8.5	6	6.3	-6.8
Zn	43.4	2.2	5.1	44	43	0.9
Ga	0.27	0.05	18.5	0.9	-	
As	0.55	0.11	20.0	0.47	0.45	18.2
Rb	22.8	1	4.4	23	-	
Sr	10.2	0.5	4.9	10.5	10	2.0
Y	0.31	0.03	9.7	0.28	-	
Mo	0.21	0.04	19.1	0.205	0.2	4.8
Cd	0.25	0.04	16.0	0.28	0.28	-12.0
Sb	0.21	0.022	10.6	0.265	0.29	-40.1
Te	<0.03	-		<0.08	-	
Cs	0.37	0.029	8.0	0.39	-	
Ba	20.7	1.1	5.3	21.2	19	8.2
La	0.58	0.05	8.6	0.51	-	
Hg	0.08	0.03	37.5	0.23	-	
Tl	0.08	0.008	9.6	0.106	-	
Pb	17.5	0.8	4.6	21.3	19	-8.6
Bi	0.05	0.005	10.9		-	
Th	0.14	0.03	21.4	0.054	-	
U	0.06	0.006	10.7	0.05	-	

a) The ICPMS/certified-value expresses the deviation in % between the results obtained by ICPMS and the certified value.

Table 6: Coefficients for linear regression analysis of the ICPMS- and INAA-data in Figure 1 (the results for ICPMS expressed as dependent variable (Y)). All results were expressed in µg g^{-1} prior to calculations.

	Range	Slope	St. dev.	Intercept	St. dev.	Corr. coeff.
	µg g^{-1}	a	S_a	b	S_b	R^2
Cr	0.3 - 24	0.52	0.075	0.33	0.16	0.38
Fe	120 - 18000	0.98	0.012	-62	20	0.976
Co	0.05 - 14	1.06	0.012	-0.04	0.01	0.982
Zn	10 - 730	0.79	0.015	8.6	1.1	0.944
As	0.01 - 2.5	0.93	0.040	-0.01	0.021	0.777
Sb	0.01 - 1.2	0.60	0.029	0.03	0.007	0.734

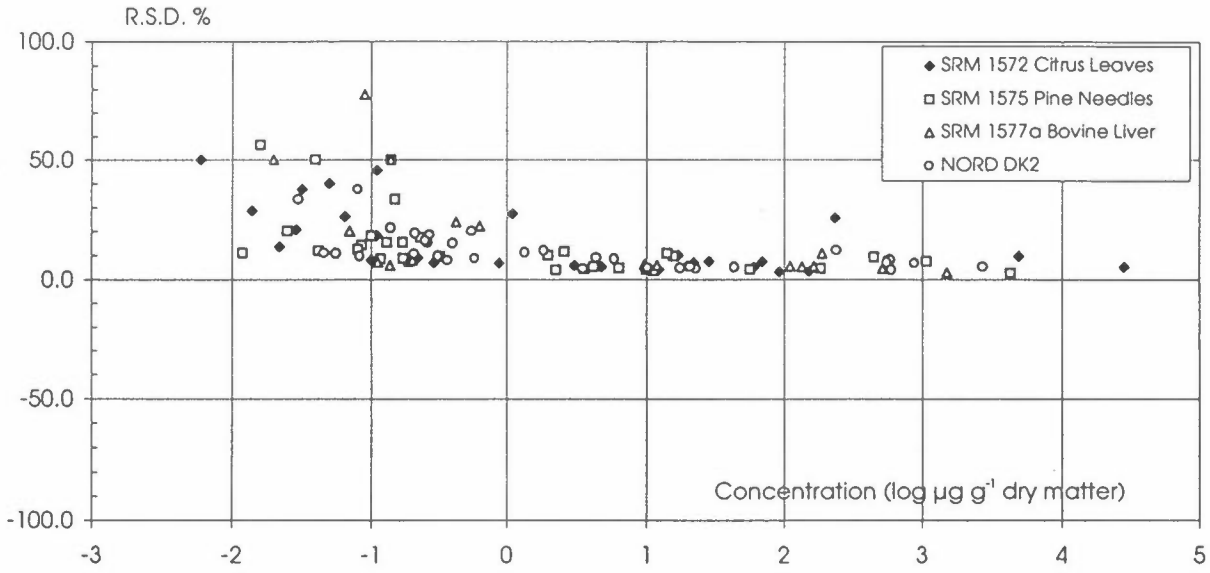

Figure 1: Precision obtained by the ICPMS-determination of elements in the four reference materials analyzed. See Table 2 - 5 for details about the precision estimates for the different elements.

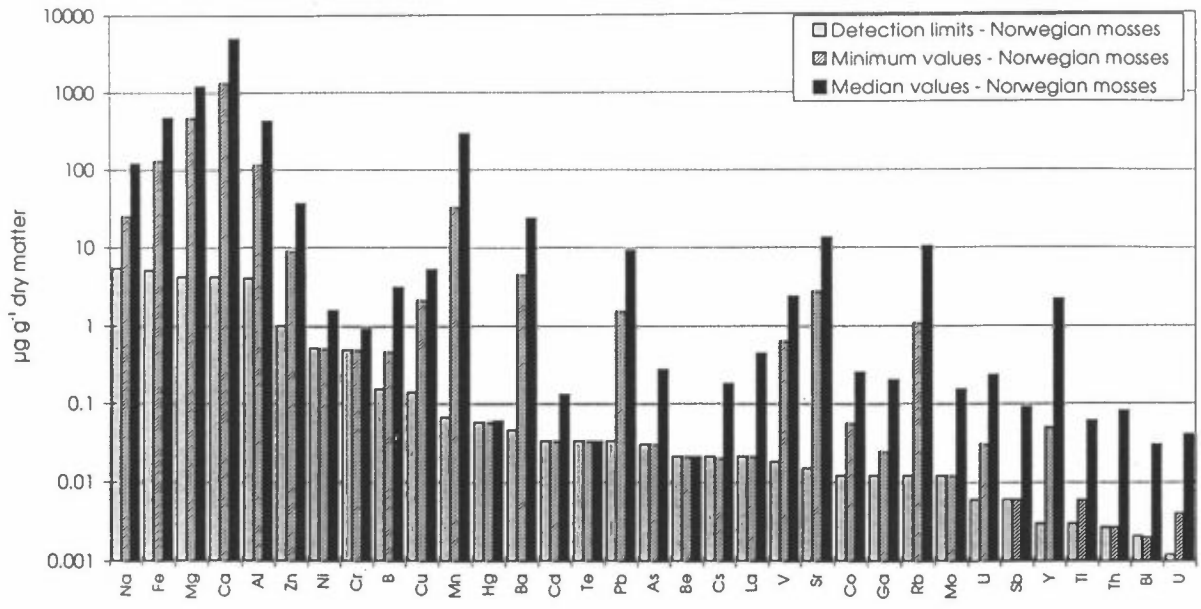

Figure 2a:Detection limits obtained by the use of the Teflon bombs (see 2.3 for details) compared to the minimum and median values from the Norwegian mosses.

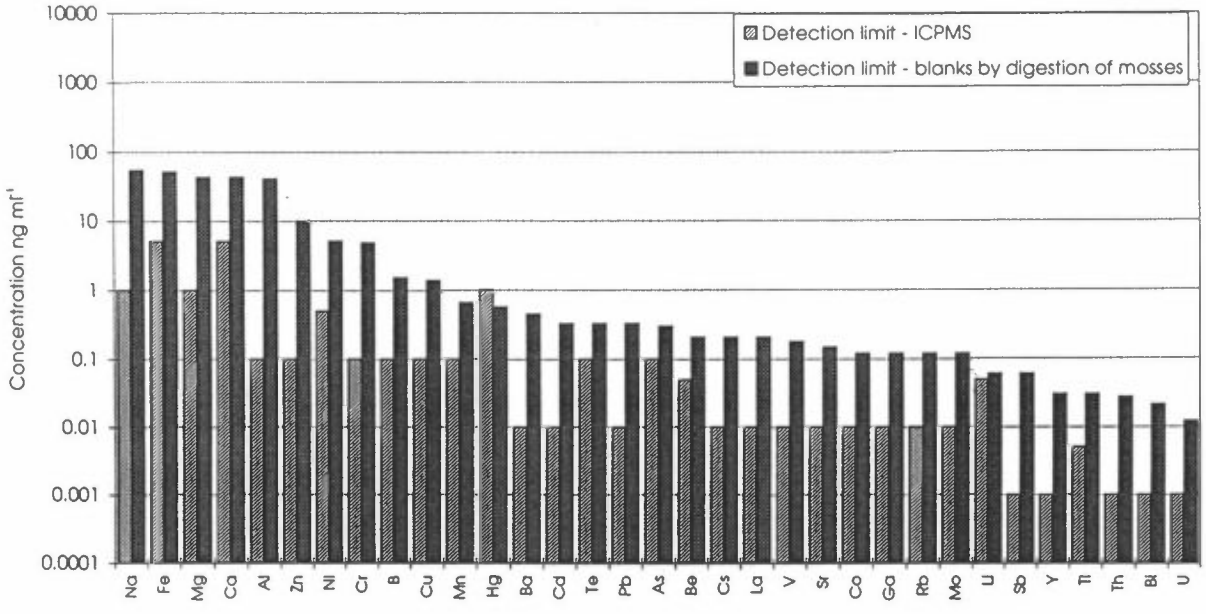

Figure 2b:Detection limits obtained by the use of the Teflon bombs (see 2.3 for details) compared to the practical detection limits for the ICPMS-technique. Note that the detection limits for the bombs are expressed in the concentration unit ng ml^{-1} (in a digest volume of 50 ml) for ease of comparison with the practical detection limits for ICPMS

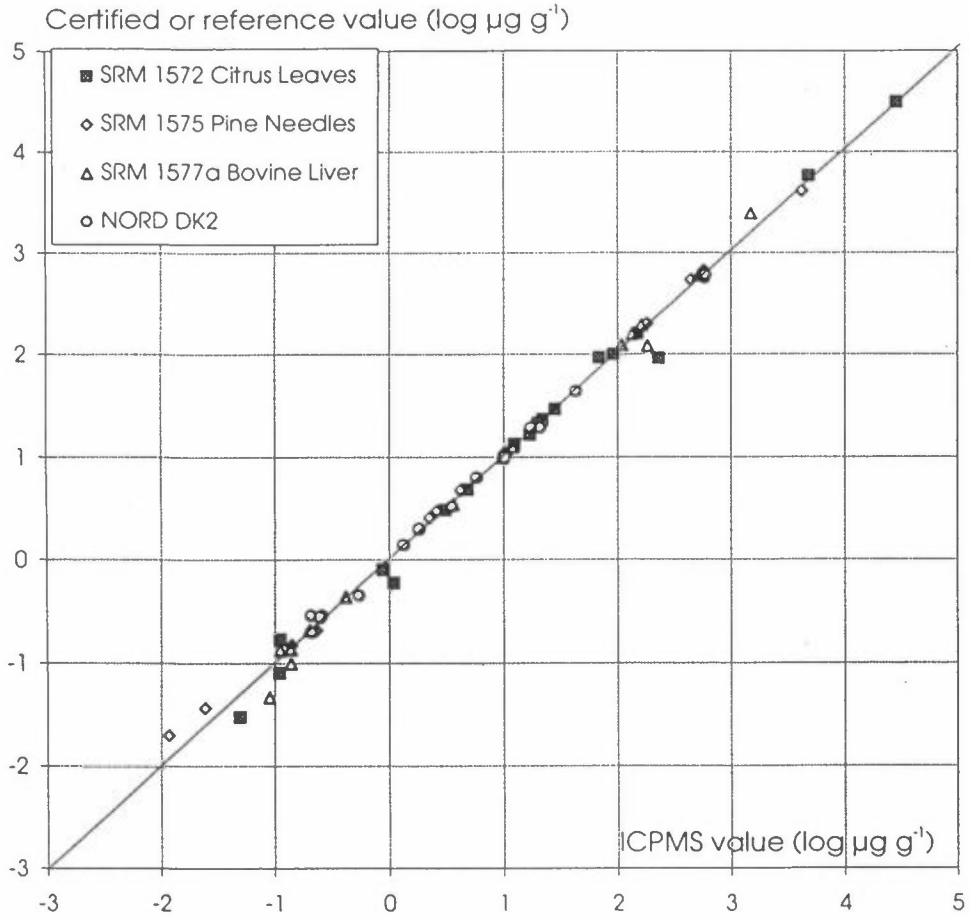

Figure 3: Results for the determination of elements by ICPMS in the standard reference materials compared to the certified values.

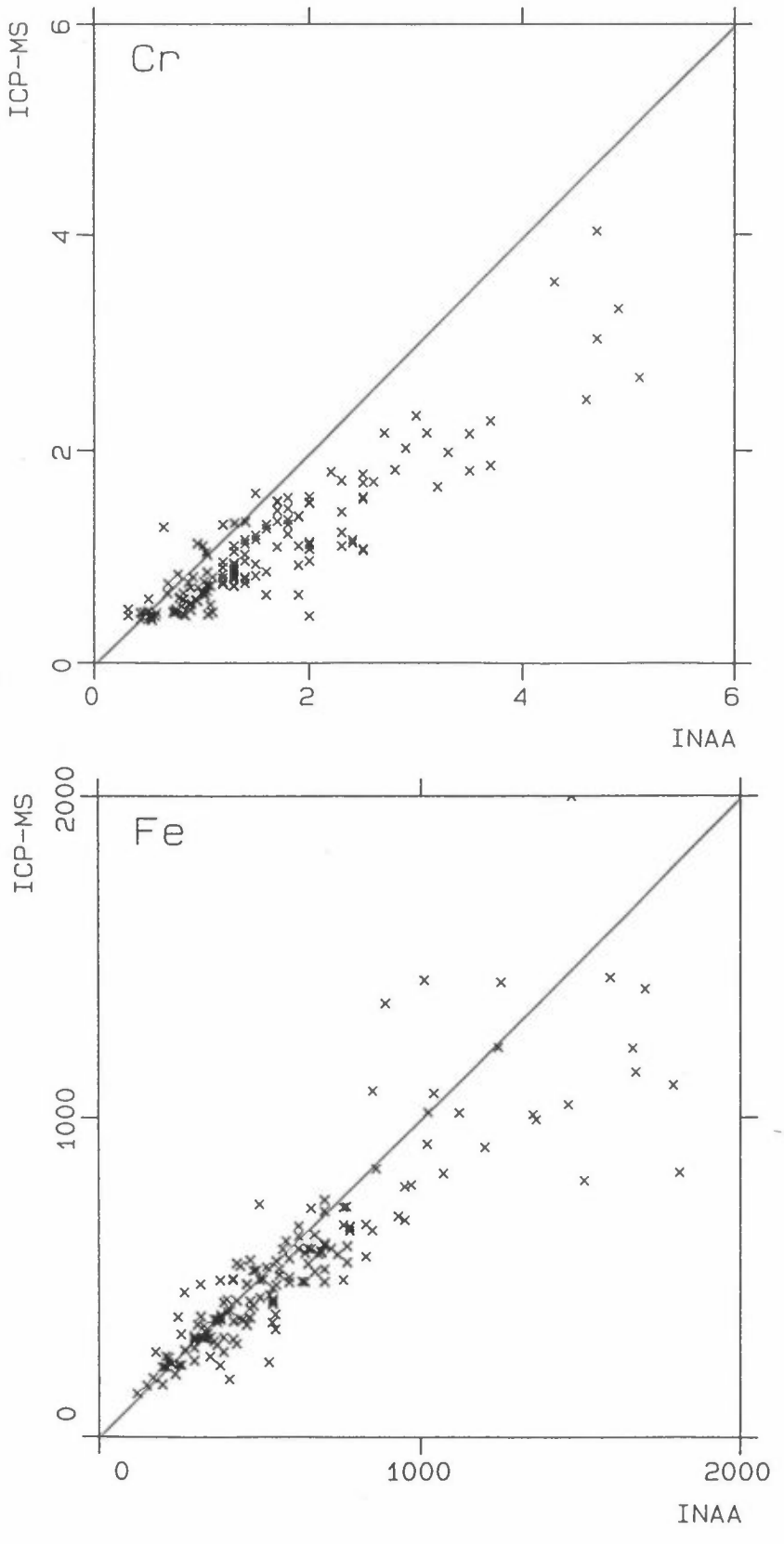

Figure 4a: Comparison of ICPMS and INAA for the determination of Cr and Fe in 150 moss samples. Results in μg g^{-1}.

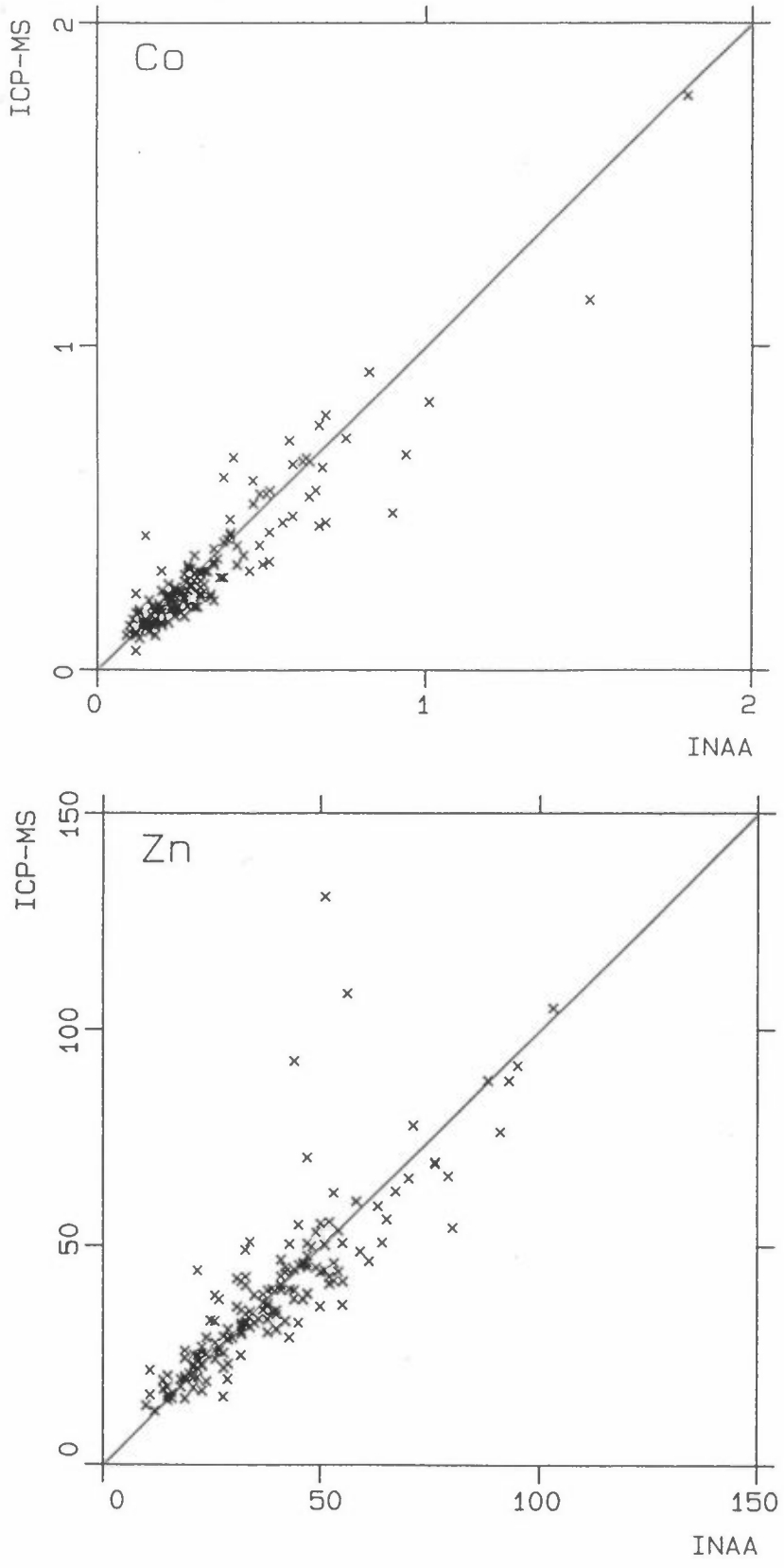

Figure 4b: Comparison of ICPMS and INAA for the determination of Co and Zn in 150 moss samples. Results in µg g^{-1}.

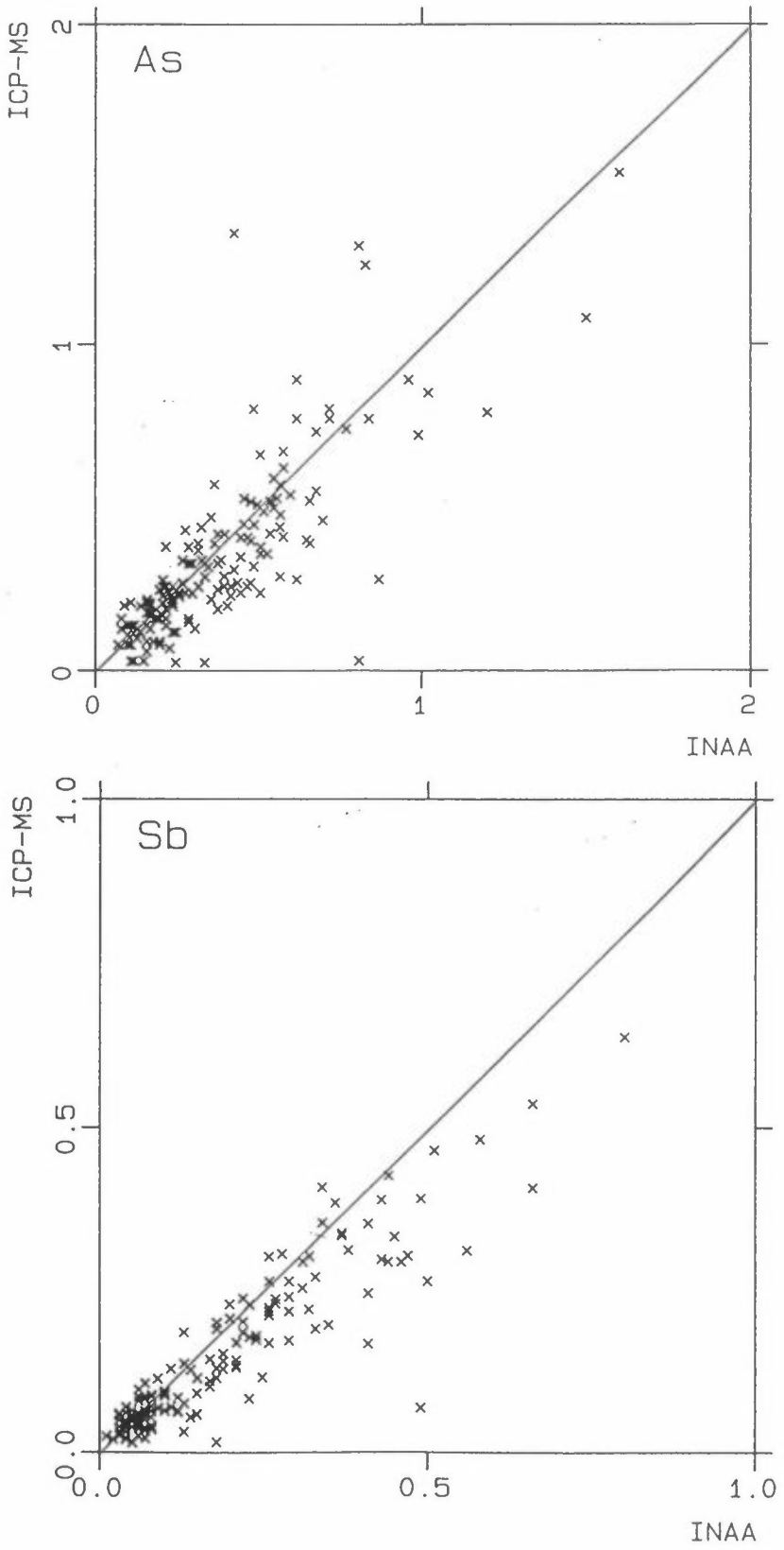

Figure 4c: Comparison of ICPMS and INAA for the determination of As and Sb in 150 moss samples. Results in µg g^{-1}.

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ABSTRACT

The analysis techniques ICPMS is studied for the determination of major and trace elements in mosses used as biomonitors for atmospheric trace metal deposition. Good accuracy and precision are documented by analysis of four certified reference materials. A comparison of ICPMS with INAA for six elements was also performed.

NORWEGIAN TITLE

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KEYWORDS		
ICPMS, INAA trace metals, mosses	Atmospheric trace metal deposition	Biomonitors

ABSTRACT (in Norwegian)

Analyseteknikken ICPMS har blitt studert for bestemmelse av hovedelementer og sporelementer i mose benyttet som biomonitorer for spormetalldeposisjon fra atmosfæren. Ved analyse av sertifiserte refereansematerialer er det dokumentert god nøyaktighet og presisjon. En sammenlikning av ICPMS med INAA ble også utført for seks elementer.

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