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Reference Material IAEA 413: Major, Minor and Trace Elements in Algae

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REFERENCE MATERIAL IAEA 413:
MAJOR, MINOR AND TRACE ELEMENTS IN ALGAE

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FOREWORD

Reference materials are a basic requirement for any sort of quantitative chemical and radiochemical analysis. Laboratories need them for calibration and quality control throughout their analytical work.

The IAEA started to produce reference materials in the early 1960s to meet the needs of the analytical laboratories in its Member States that required reference materials for quality control of their measurements. The initial efforts were focused on the preparation of environmental reference materials containing anthropogenic radionuclides for use by those laboratories employing nuclear analytical techniques. These reference materials were characterized for their radionuclide content through interlaboratory comparison involving a core group of some 10 to 20 specialist laboratories. The success of these early exercises led the IAEA to extend its activities to encompass both terrestrial and marine reference materials containing primordial radionuclides and trace elements.

Today, the IAEA has more than 90 reference materials and maintains a customer base of about 5000 members from more than 85 Member States.

Within the frame of IAEA activities in production and certification of RM, this report describes the certification of the IAEA 413: Major, minor and trace elements in algae. Details are given on methodologies and data evaluation.

The IAEA officer responsible for this publication was A. Shakhashiro of the IAEA Environment Laboratories.

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CONTENTS

1. INTRODUCTION

A reliable determination of toxic elements in environmental samples plays a vital role in the assessment of environmental pollution. Appropriate assessment depends on the careful selection of representative samples that truly reflect pollution levels. Biomonitors, such as lichen and algae, are examples of environmental samples that have been widely used by the scientific community to monitor environmental pollution. The second pillar supporting reliability of environmental measurements is the availability of appropriate reference materials for analytical quality control and method validation. Besides IAEA-392, IAEA 413 is another algal material prepared for this aim.

Reference values for the mass fractions and associated standard uncertainties have been established for: As (127 ± 6.6 mg/kg), Ca (3143 ± 112 mg/kg), Cd (204 ± 8.5 mg/kg), Co (4.24 ± 0.25 mg/kg), Cr (377 ± 14 mg/kg), Fe (1370 ± 39 mg/kg), K (10740 ± 270 mg/kg), Mg (4058 ± 117 mg/kg), Mn (158 ± 3.4 mg/kg), Na (375 ± 20 mg/kg), Ni (113 ± 4.9 mg/kg, Pb (242 ± 7 mg/kg), Zn (169 ± 3.3 mg/kg).

For Cu (11.1 ± 1.0 mg/kg) and Hg (53.2 ± 4.0 mg/kg) information values are reported.

During sample production and certification, the requirements for reference material production and certification as stated in ISO guides 34 and 35 [1, 2] were taken into account. This report summarizes the preparation and certification process.

The input, support and fruitful discussion with all analysts: E. de Nadai Fernandes, P. Ostapczuk, E. Benetka, P. Bode, M. Campbell, S. Bamfort and M. Makarewicz, as well as with U. Sansone, and P. Martin is highly appreciated.

2. DESCRIPTION OF ALGAE MATERIAL

The IAEA-413 algae material was prepared by the Terrestrial Environment Laboratory of the International Atomic Energy Agency's in cooperation with the Institute of Microbiology, Academy of Sciences of the Czech Republic in Trebon.

The IAEA-413 algae material (type: Chlorella Boehm) was produced under standard outdoor culture conditions. The sloped bioreactor bed was constructed from steel. Mineral nutrients were prepared from chemicals and added as required for an optimal growing. The amount of elements added to the nutrient solution was adjusted to allowing bioaccumulation without poisoning the algae [3, 4].

After harvesting, the algae were transferred to a cooled tank and continuously spray dried with moderate venting and at a moderate temperature, avoiding damage to the cell structure.

A two kilograms sample of the dry bulk algae material was irradiated with γ rays to improve long-term stability of the material by reducing microbiological action. Based on the particle size measurements it could be verified that the single cell structure of the algae had been maintained during preparation. Although the natural single cell particle size was around 4.6 μm, the average particle size measured using the Martin's diameter method increased to about 8 or 16 μm due to conglomeration.

Bottling of IAEA-413 was done under normal laboratory conditions, taking all precautions to avoid segregation. After bottling, the samples were packed into plastic bags, sealed, and sterilized by gamma ray irradiation with a total dose of 25 kGy using a Co-60 source.

2.1.Homogeneity study

The homogeneity of the material was tested twice, directly after bottling and during the characterization exercise. Sample bottles covering the whole bottling range were randomly selected for homogeneity tests and the characterization. During the homogeneity tests emphasis was placed on performing measurements under good repeatability conditions.

Table 1 shows the relative repeatability standard deviation (RSD%) of INAA measurements obtained for 15 bottles. The bottle selection was random and covered the whole bottle number range. The sample mass used as test portion was 10 mg.

TABLE 1: RELATIVE STANDARD DEVIATIONS OBTAINED DURING IAEA-413 HOMOGENEITY MEASUREMENTS

Element	As	Br	Cd	Co	Cr	Fe	Hg	Na	Zn
RSD %:	1.17	1.18	1.24	2.49	0.94	2.25	1.55	1.13	1.74

The second homogeneity tests for IAEA 413 covered all elements for which reference and information values have been assigned. The results reported in Table 2 were derived from 2 to 3 sub-samples from 6 bottles analysed under repeatability conditions during the characterization campaign. The sample portion was in all cases about 100 mg or less.

The standard uncertainty associated with the material heterogeneity was calculated using the formulas stated in ISO Guide 35 [2]. Two approaches, ANOVA (formulas 1 and 2), and 'taking into account insufficiently good measurement repeatability' (formula 3) were used. The latter calculation method was used in addition since some bottles gave negative values for the between-bottle variance.

$$s_{wb}^2 = MS_{within} \tag{1}$$

$$s_{bb}^2 = \frac{MS_{among} - MS_{within}}{n_0} \tag{2}$$

$$u^*_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt[4]{\frac{2}{\nu_{MS_{within}}}} \tag{3}$$

The abbreviations are explained in the list of abbreviations.

The uncertainties due to sample heterogeneity were generally very small and confirmed the results from the first INAA data (Table1).

TABLE 2: GENERAL STATISTICS AND THE UNCERTAINTY DUE TO HETEROGENEITY TAKING INTO ACCOUNT A SINGLE METHOD AND ABOUT 100 mg SAMPLE MASS

Element	n_b/n_R	s.e.m. [%]	F_{test}	Method applied	s_{bb} [%]	u^*_{bb} [%]	Reported method u[%] k=1
As	6/3	0.25	yes (99%)	INAA	0.55	0.39	1.64
Ca	6/2	0.21	yes	INAA	neg	1.42	1.88
Cd	6/3	0.10	yes	INAA	0.80	2.86	2.40
Co	6/3	0.07	yes	INAA	0.30	0.46	1.20
Cr	6/3	0.05	yes	INAA	0.55	0.30	1.45
Cu	6/2	0.28	yes	ICP-MS	2.18	1.42	no info
Fe	6/3	0.09	yes	INAA	0.83	0.53	1.34
Hg	6/3	0.15	yes	INAA	1.62	0.79	2.02
K	6/2	0.14	yes	INAA	0.51	0.87	0.94
Mg	6/2	0.06	yes	ICP-MS	0.28	0.37	no info

Element	n_b/n_R	s.e.m. [%]	F_{test}	Method applied	s_{bb} [%]	u^*_{bb} [%]	Reported method u[%] k=1
Mn	6/2	0.11	yes	INAA	0.55	0.62	0.65
Na	6/3	0.05	yes	INAA	neg	0.34	2.37
Ni	6/3	0.14	yes	INAA	0.80	0.89	2.06
Pb	6/2	0.09	yes	ICP-MS	0.64	0.48	1.31
Zn	6/3	0.09	yes	INAA	0.80	0.49	1.32

The facts that the standard errors of the mean (s.e.m.) were below 0.28 % for all elements, and all data sets of the homogeneity study showed normal distribution and had no outlying results, gave additional evidence on the good homogeneity of the material. These data also confirmed that the analytical methods were under control and suitable for the homogeneity test.

The uncertainties associated with the sample heterogeneity (s_{bb} and u^*_{bb}) reported in Table 2 can be used as additional information. They are referring to a defined test portion measured with a stated analysis technique while the certification is taking into account the in-bottle and between-bottle variances of all participating laboratories (see section 5: Evaluation of results). The component of the combined uncertainty of the certification associated with the material heterogeneity cannot be linked to a specific mass of the test portion but is covering a mass range.

During a co-ordinated research project (CRP) on “Reference Materials for Microanalytical Nuclear Techniques” it could be demonstrated that IAEA 413 Algae showed good homogeneity for K, Cr, Mn, Fe, Zn, As, Br and Cd even for a 1 mg test portion [5,6].

Although there are indications that due to the natural small particle size of this material the homogeneity of the material is generally suitable even for smaller test portions, it is recommended that the minimum test portion used for analysis should be 100 mg. If smaller test portion is taken the uncertainty of the property value should be expanded taking into account the relationship of mass and heterogeneity explained in the concept of Ingamels sampling constant or other related concepts [7,8,9].

2.2. Long-term stability

The long-term stability was measured for 10 elements. Storage temperatures of 40, 20, 4 and -20 °C were tested. Test time was about 3 years and ten (n = 10) independent determinations were performed for the four temperature conditions.

Applying the F-test and t-tests for the 10 results, the long term reproducibility showed equal variances for all four data sets. In addition the t-tests assured that there was no significant difference on the analysis results of all tested elements for the four storage conditions.

For the trend analysis, the slope (b_1), intercept (b_0) and the uncertainties of both parameters were calculated (s_{b1}, s_{b0}). Table 3 shows the results of the trend analysis of samples stored at room

temperature (about 20 ^{o}C ± 5 ^{o}C) during 1027 days. Five measurements were performed during the first 100 days, and then the measurement intervals were extended to approximately 6 months.

For the calculation of all parameters the equations as described in ISO Guide 35 [2] Chapter 8.3.1 were used. The critical value was calculated:

$$\text{Critical value} = t_{0.95,n-2} * sb_1 \quad (4)$$

The trend would be significant if the slope (b_1) was bigger than the critical value. Since the critical value was always higher, the trend is insignificant. As a consequence it may be stated that no degradation was observed.

TABLE 3: RESULTS OF THE TREND CALCULATION FOR IAEA 413

	n	b_1	sb_1	b_0	sb_0	Critical value (95% conf.)	Significant trend
Fe	10	0.0293	0.1159	1453.2	48.17	0.2674	no
Cu	10	0.0006	0.0009	10.70	0.39	0.0020	no
Co	10	0.0002	0.0004	4.16	0.15	0.0008	no
Cr	10	0.0191	0.0184	372.1	7.6	0.0423	no
Mn	10	-0.0051	0.0125	167.7	5.2	0.0289	no
Ni	10	0.0003	0.0050	114.7	2.1	0.0115	no
Zn	10	0.0086	0.0139	163.6	5.8	0.0320	no
As	10	0.0047	0.0060	126.3	2.5	0.0139	no
Cd	10	-0.0083	0.0111	203.8	4.6	0.0257	no
Pb	10	0.0163	0.0094	245.1	3.1	0.0262	no

It was decided not to include the uncertainty related to the stability study, since the measurement reproducibility standard deviation within the three years of the study was large and would lead to an overestimation of the combined uncertainty. The long-term stability of the material is further monitored using an isochronic approach.

3. CHARACTERIZATION

For the characterization exercise, laboratories were selected based on their successful participation in previous IAEA intercomparison runs. All of them had an implemented quality assurance system conforming to ISO 17025, but not all were formally accredited at the time of the exercise.

During the planning meeting, a short guideline was prepared where quality aspects (e.g. traceability of standards and calibration, instrument and balance performance, quality of pipettes and volumetric flasks) and analytical requirements (e.g. number of sub-samples, test portion mass, dissolution techniques) were defined [10].

Each analyst had received 6 bottles of the algae material (randomly selected covering the whole bottling sequence) and was requested to analyze from each bottle at least 2 sub-samples following the established guidelines.

Test portion mass for the analysis was proposed to be 100 mg (if feasible, to achieve a good limit of detection). To assess whether some elements are silicate bound, the IAEA laboratories performed two dissolution techniques one of them applying HF. Both sets of dissolved samples were measured under repeatability conditions. Results obtained using ICP-OES are shown in Table 4. No significant difference (95% conf.) of the elemental mass fractions measured could be detected.

TABLE 4: ICP-OES RESULTS USING TWO DIFFERENT DIGESTION PROCEDURES (*FOR POTASSIUM INSTEAD OF $HClO_4$, H_2O_2 AND AAS WAS USED)

	PMW HNO_3, $HClO_4$, HF			PMW HNO_3, $HClO_4$			Δ	±Δ%
Element	Mass fraction ± u [mg/kg]			Mass fraction ± u [mg/kg]				
As	126	±	6	127	±	5	0.9	0.70
Ca	3121	±	87	3133	±	111	12	0.38
Cd	200	±	3	201	±	3	1	0.52
Co	4.1	±	0.3	4.0	±	0.3	0.1	2.6
Cr	373	±	6	377	±	7	4	1.0
Cu	10.8	±	0.4	10.7	±	0.6	0.1	1.2
Fe	1359	±	28	1372	±	22	13	0.9
Hg	No data available							
K*	10686	±	171	10697	±	174	11	0.11

	PMW HNO_3, $HClO_4$, HF			PMW HNO_3, $HClO_4$			Δ	±Δ%
Element	Mass fraction ± u [mg/kg]			Mass fraction ± u [mg/kg]				
Mg	4122	±	59	4121	±	103	1	0.03
Mn	155	±	2	157	±	2	2	0.89
Ni	110	±	3	111	±	2	1	1.1
Pb	231	±	5	233	±	4	2	0.56
Zn	165	±	5	165	±	4	0	0

Tables 5.1 to 5.15 give a short summary for all elements on the dissolution procedures used before analysis, and the analytical method applied. The abbreviations are explained on page 25.

It is worth mentioning that all digestion methods were using strong oxidizing acids, acid mixtures or pressure, or a combination of all.

TABLE 5.1 ARSENIC

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P6/5	200	HPD at 300 °C, HNO_3	HG- AAS, 193.7 nm
P2/1a	100	PMW HNO_3, H_2O_2	ICP-MS, Mass 75
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 193.695 nm
ND/1	NA	Non destructive	ED-XRF, As-K_α
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES axial, 188.979 nm
ND/2	100	Non destructive	INAA, ^{76}As at 559 keV
P2/1	100	PMW HNO_3, H_2O_2	ET AAS , 193.7 nm
ND/3	150	Non destructive	INAA [1] [11]
P1/1	100	PMW, HNO_3,	ICP-MS, Mass 75

[1] Laboratory ND/3 used for the identification and quantification of each element all gamma ray lines, including sum-peaks of all radionuclides produced upon reactor neutron irradiation from the respective stable isotopes of that element. The radionuclides, gamma-ray lines and intensity ratios are traceable to M.Blaauw [11].

TABLE 5.2 CALCIUM

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 393.367 nm
P8/5	200	PTFE at 180 °C, HNO_3	ICP-OES, 422.673 nm
ND/1	NA	Non destructive	ED-XRF, Ca-K_α
P2/1	100	PMW, HNO_3, H_2O_2	Flame AAS, 422.7 nm
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES axial 422.673 nm
P2/1a	100	PMW, HNO_3, H_2O_2	ICP-MS, mass 44
ND/3	150	Non destructive	INAA [11]

TABLE 5.3 CADMIUM

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P8/5	200	PTFE at 180 °C, HNO_3	ICP-OES, 226.502 nm
P2/1a	100	PMW, HNO_3, H_2O_2	ICP-MS, mass 114
ND/3	150	Non destructive	INAA [11]
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 226.502 nm
ND/1	100	Non destructive	INAA, ^{115}Cd, 336.2 and 527.9 keV
P2/1	100	PMW, HNO_3, H_2O_2	Flame AAS
ND/2	100	Non destructive	INAA, ^{115}Cd, 336.2 and 527.9 keV
ND/1	NA	Non destructive	ED-XRF, Cd-K_α
P1/1	100	PMW, HNO_3	ICP-MS, mass 111
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES, 228.802nm

TABLE 5.4 COBALT

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 228.616 nm
P6/5	200	HPD at 300 °C, HNO_3	ASV (Square Wave Detection)
ND/2	100	Non destructive	INAA, ^{60}Co, 1173 and 1333 keV
ND/1	100	Non destructive	INAA, ^{60}Co, 1173 and 1333 keV
ND/3	150	Non destructive	INAA* [11]
P2/1a	100	PMW HNO_3, H_2O_2	ICP-MS, mass 59
P2/1	100	PMW HNO_3, H_2O_2	ET AAS, 242.5nm
P1/1	100	PMW, HNO_3,	ICP-MS, mass 59

TABLE 5.5 CHROMIUM

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 267.716 nm
P8/5	200	PTFE at 180 °C, HNO_3	ICP-OES, 267.716 nm
ND/2	100	Non destructive	INAA, ^{51}Cr, 320.1 keV
ND/1	100	Non destructive	INAA, ^{51}Cr, 320.1 keV
ND/1	NA	Non destructive	ED-XRF, Cr-K_α
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES, 205.552 nm
P2/1a	100	PMW HNO_3, H_2O_2	ICP-MS, mass 53
P2/1	100	PMW HNO_3, H_2O_2	Flame AAS, 242.5 nm
ND/3	150	Non destructive	INAA * [11]
P1/1	100	PMW, HNO_3,	ICP-MS, mass 53

TABLE 5.6 COPPER

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 324.754 nm
P8/5	200	PTFE at 180 °C, HNO_3	ICP-OES, 327.396
P2/1	100	PMW, HNO_3, H_2O_2	ET AAS, 324.8 nm
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES axial, 327.396 nm
P1HF/1	100	PMW, HNO_3, HF	ICP-MS, mass 63

TABLE 5.7 IRON

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 259.940 nm
P8/5	200	PTFE at 180 °C, HNO_3	ICP-OES, 259.940 nm
ND/2	100	Non destructive	INAA, ^{59}Fe, 1099 and 1292 keV
P2/1	200	PMW, HNO_3, H_2O_2	Flame AAS, 248.3 nm
P2/1a	100	PMW, HNO_3, H_2O_2	ICP-MS, mass 57
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES , 238.204 nm
ND/3	150	Non destructive	INAA * [11]
P1/1	100	PMW, HNO_3,	ICP-MS, mass 57
ND/1	100	Non destructive	INAA, ^{59}Fe, 1099 and 1292 keV

TABLE 5.8 POTASSIUM

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
ND/1	NA	Non destructive	ED-XRF, K-K_α
ND/3	150	Non destructive	INAA* [11]
P8/5	200	PTFE at 180 °C, HNO_3	ICP-OES, 769.898 nm
ND/2	100	Non destructive	INAA, ^{42}K, 1525 keV
P2/1	100	PMW, HNO_3, H_2O_2	Flame AAS, 769.9 nm
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES, 769.896 nm

TABLE 5.9 MAGNESIUM

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 279.553 nm
P1HF/1	100	PMW, HNO_3, HF	ICP-MS, mass 24
P8/5	200	PTFE at 180 °C, HNO_3	ICP-OES, 279.553 nm
P2/1	100	PMW, HNO_3, H_2O_2	Flame AAS, 202.6 nm
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES, 285.213 nm

TABLE 5.10 MANGANESE

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 257.610 nm
P1/1	100	PMW, HNO_3,	ICP-MS, mass 55
ND/3	150	Non destructive	INAA * [11]
P2/1	100	PMW, HNO_3, H_2O_2	Flame AAS, 279.8 nm
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES, 257.610 nm
P2/1a	100	PMW, HNO_3, H_2O_2	ICP-MS, mass 55
P8/5	200	PTFE at 180 °C, HNO_3	ICP-OES, 257.610 nm

TABLE 5.11 MERCURY

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P7/4	1000	reflux, HNO_3	CV AAS
ND/2	100	Non destructive	INAA, ^{203}Hg, 279.2 keV
ND/3	150	Non destructive	INAA * [11]
P5/5	300	LPD, HNO_3	CV AAS, with amalgam accumulation
P1/1	100	PMW, HNO_3,	ICP-MS mass 202

TABLE 5.12 SODIUM

Prep/Lab Code	Approx. test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P2/1	200	PMW, HNO_3, H_2O_2	Flame AAS, 589.0 nm
ND/3	150	Non destructive	INAA * [11]
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES, 589.592 nm
P8/5	200	PTFE at 180 °C, HNO_3	ICP-OES, 589.592 nm
ND/2	100	Non destructive	INAA, ^{24}Na, 1369 keV

TABLE 5.13 NICKEL

Prep/Lab Code	Approx. .test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P2/1	100	PMW, HNO_3, H_2O_2	ET AAS, 232.0 nm
P1/1	100	PMW, HNO_3,	ICP-MS, mass 60
ND/1	100	Non destructive	INAA, ^{58}Co, 811 keV
P2/1a	100	PMW, HNO_3, H_2O_2	ICP-MS, mass 60
ND/2	100	Non destructive	INAA, ^{58}Co, 811 keV
ND/3	150	Non destructive	INAA * [11]
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES, 231.604 nm
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 221.647 nm
P6/5	200	HPD at 300 °C, HNO_3	ASV

TABLE 5.14 LEAD

Prep/Lab Code	Approx. .test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P2/1	100	PMW, HNO_3, H_2O_2	ET AAS, 283.3 nm
P1/1	100	PMW, HNO_3,	ICP-MS, mass 208
ND/1	NA	Non destructive	ED-XRF, Pb-L_α
P2/1a	100	PMW, HNO_3, H_2O_2	ICP-MS, mass 208
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES axial, 231.604 nm
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 220.353 nm
P8/5	200	PTFE at 180 °C, HNO_3	ICP-OES, 220.353 nm

TABLE 5.15 ZINC

Prep/Lab Code	Approx. .test portion mass [mg]	Dissolution technique/ Acid(s)	Analysis technique
P2/1	100	PMW, HNO_3, H_2O_2	Flame AAS, 213.9 nm
P3/1	1000	PMW, HNO_3, $HClO_4$	ICP-OES, 206.200 nm
P2/1a	100	PMW, HNO_3, H_2O_2	ICP-MS, mass 64
ND/1	NA	Non destructive	ED-XRF, Zn-K_α
ND/2	100	Non destructive	INAA, ^{65}Zn, 1116 keV
P4/4	1000	open, HNO_3, $HClO_4$	ICP-OES, 213.856 nm
ND/3	150	Non destructive	INAA * [11]
P1/1	100	PMW, HNO_3	ICP-MS, mass 64

4. EVALUATION OF RESULTS

4.1. General

All results were collected and used as a basis for discussion. During the characterization meeting, analytical results were rejected based on the following conditions:

- if there were technically justified doubts on the analytical quality, or
- where analysts had used two different digestion methods to evaluate the complete dissolution of the sample and the measurement technique was the same, the analysts were asked to withdraw one set of data. This was to avoid the double counting of methods using dissolution techniques in the evaluation.

For some elements, non-destructive analytical techniques were not available. But since the dissolution methods were independent and very different, and elements were not silica bound (see Table 4), it is assumed that no bias was introduced which could be based on incomplete dissolution.

4.2. Statistical screening of the combined data sets

Since the number of data sets was small for many elements (e.g. n=5), their statistical evaluation was expanded to cover all individual results of all methods and analysts and not only the laboratory mean values. The HISTO program was utilized for this purpose. HISTO is a software package developed by the Chemistry Unit of the Terrestrial Environment Laboratory for statistical evaluation of data. Beside general descriptive statistics, the following tests are included in the program:

- Outlier tests (Dixon, Grubbs, Skewness, Kurtosis)
- Directional tests (Skewness, Kurtosis)
- Normality tests (Kolmogorov-Smirnov, Kolmogorov-Smirnov-Lilliefors)

TABLE 6: INFORMATION ON THE STATISTICAL DATA EVALUATION

Element	n_L	Method used	n_i	$n_{outlier}$	Normal distribution	s_i [%]	s.e.m.[%]
As	10	INAA (3), HG-AAS, ICP-OES (2), AAS, XRF, ICP-MS (2)	137	0	yes (99%)	5.40	0.46
Ca	7	INAA, AAS, ICP-OES(3), XRF, ICP-MS	84	0	yes	3.26	0.36
Cd	10	INAA(3), ICP-OES(3), AAS, XRF, ICP-MS(2)	120	0	yes (99%)	4.01	0.37
Co	8	INAA(3), ICP-OES, ASV, AAS, ICP-MS(2)	114	0	yes (99%)	4.52	0.42
Cr	10	INAA(3), ICP-OES, AAS, XRF, ICP-MS(2)	132	0	yes	3.28	0.29
Cu	5	ICP-OES(3), AAS, ICP-MS	60	0	no	3.87	0.50
Fe	9	INAA(3), ICP-OES(3), AAS, ICP-MS(2)	125	2	yes	3.47	0.31
Hg	5	INAA(2), AAS CV(2), ICP-MS	65	1	yes (99%)	5.73	0.71
K	6	INAA(2), ICP-OES(2), AAS, XRF	78	0	yes	2.35	0.27
Mg	5	ICP-OES(3), AAS, ICP-MS	60	0	yes	2.50	0.32
Mn	7	INAA(1), ICP-OES(3), ICP-MS (2), AAS	84	1	yes	2.79	0.30
Na	5	INAA(2), ICP-OES(2), AAS	66	0	yes (99 %)	4.16	0.51
Ni	9	ICP-OES(2), AAS, ICP-MS(2), ASV, INAA(3)	126	0	yes	4.94	0.44
Pb	7	ICP-OES(3), AAS, ICP-MS(2), XRF	84	0	yes	2.67	0.29
Zn	8	INAA(2), ICP-OES(2), AAS, XRF, ICP-MS (2)	102	2	yes	2.27	0.22

The standard deviation (s_i) of all individual measurements (n_i) was below 6 % (average 3.6 %) and standard error of the mean (s.e.m) was below 0.71 %. Nearly no outlying data were observed. The directional tests did not always pass the acceptance criteria but still the Kolmogorov-Smirnov and Kolmogorov-Smirnov-Lilliefors normality tests showed normal distributions of the data sets except for Cu.

4.3. Calculation of property value and associated uncertainty

The property values of all elements were established on the basis of a robust approach proposed by David L. Duewer [14] and the Mixture Model Median (MM-median) of the analytical results reported by the expert laboratories was calculated. The MM-median is a direct analogue of the median. It is the location which divides the Mixture Model Probability Density Function (MM-PDF) into two sections of equal area. The MM-median is closely related to the median. It is robust to outliers and also accounts for the reported uncertainty of each measurement result.

To estimate the standard uncertainty associated with the property value the MM-median based Standard Deviation S(MM-median) was calculated from the span of the central 50% of the MM-PDF density function.

Table 7 shows the assigned property values and associated standard uncertainties.

A 'reference' property value was assigned if:

- The analyte results passed the normality tests (at least at 99 % confidence level);
- The number of statistical outliers in the data sets was below 5%;
- The maximum standard uncertainty was below the in-house established limits:

Mass fraction range [mg/kg]	Maximum u (%)
1-25	10
25-100	8
>100	6

The variances in Table 7 (within-bottle (S^2_{wb}), between-bottle (S^2_{bb}), and between laboratory (S^2_{bL})) obtained from the fully nested ANOVA. This is one approach listed in the ISO guide 35. All related formulas can be found in Annex A of the guide [2].

TABLE 7: REFERENCE MASS FRACTIONS AND STANDARD UNCERTAINTIES [mg/kg DRY MASS] ESTABLISHED DURING THE CERTIFICATION OF IAEA 413

Element	Reference value [mg/kg]	u_{wb}	u_{bb}	u_{bL}	Combined standard uncertainty u_x
As	127	0.12	0.17	2.06	6.6
Ca	3143	5.3	5.8	33.4	112
Cd	204	0.26	0.12	2.57	8.5
Co	4.24	0.05	0.00	0.06	0.25
Cr	377	0.38	0.17	3.83	14
Fe	1370	1.84	1.77	14.73	39
K	10740	17.3	7.8	87.2	270
Mg	4058	4.8	8.3	41.1	117
Mn	158	0.29	0.13	1.40	3.4
Na	375	0.89	0.94	6.36	20
Ni	113	0.42	0.00	1.10	4.9
Pb	242	0.30	0.22	2.30	7
Zn	169	0.24	0.35	0.62	3.3

Element	Information value[mg/kg]	u_{wb}	u_{bb}	u_{bL}	Combined standard uncertainty u_x
Cu	11.1	0.03	0.01	0.17	0.5
Hg	53.2	0.14	0.13	1.45	4.0

Where:

$$u_{wb} = \frac{s_{wb}^2}{n_i}, \qquad u_{bb} = \frac{s_{bb}^2}{n_b . n_L}, \qquad u_{bL} = \frac{s_{bL}^2}{n_L}$$

For Hg no reference but only an information value was assigned since the sample dissolution sometimes showed problems which could not be clearly explained. Cu failed to be a reference value, because the data did not show a normal distribution.

4.4.Traceability of results

The property values assigned to the algae reference material are element mass fractions, expressed in the derived SI unit mg/kg. The utmost care was taken regarding the metrological traceability of the property values assigned to this reference material already at the planning phase and during the entire characterization process. Laboratories participating in the characterization campaign have been requested to carefully choose the calibrants and to provide the IAEA with all related information, including certificates. However, the selection of measurement methods and measurement procedures, as well as respective calibrants, was based on the decision of the participating laboratory. A consequence of the use of different calibrants is the fact that the metrological chain(s) for each of the assigned quantity values (combined from a number of results), cannot easily be described. Therefore, the assigned property values — the element mass fractions — although expressed in the derived SI unit, are not intended for calibration purposes, and the reference material as such is not to be used as a calibrant.

4.5. Intended use

This reference material is intended to be used for quality assurance purposes, basically as a quality control material for the measurement of the elemental composition of biological materials, especially biomonitors, for the assessment of a laboratory's analytical work and for the validation of analytical methods.

The estimated standard uncertainty is relatively large due to the consideration of the between-laboratories dispersion in the calculation of the S(MM-median). It is expected that individual laboratories applying a single analytical procedure will produce results with a smaller dispersion. Therefore it is recommended that the users establish their own reproducibility standard deviations to be used as control limits for precision.

4.6. Instructions for use

Before each sub-sampling, the bottle should be shaken thoroughly for 5 min. to re-homogenize the sample. The recommended minimum test portion size is 100 mg.

Analysts are reminded to take appropriate precautions to avoid contamination of the sample and the remaining material in the bottle.

It is recommended to store the material after the opening of the bottle in a refrigerator (at 4 to 8 °C) or dessicator. Exposure to sunlight should be avoided.

Storage at room temperature and even at temperatures up to 40 °C did not show degradation of the originally sealed algae material.

4.7. Dry mass determination

All reference and information values are expressed on a dry mass basis. Therefore the analytical results need to be corrected for the moisture content of the sample at the time of analysis.

It is recommended to dry a separate sample portion of at least 500 mg for 4 hours at 80 °C. If smaller sample test portions are taken, the uncertainty on the dry mass correction factor is increased and should be taken into account for the total uncertainty calculation. Indication of the magnitude of the dry mass uncertainties and their influence on the final results can be found in a related publication [13]. The use of a different drying procedure may lead to biases in the results and should be avoided [13].

APPENDIX
GRAPHICAL PRESENTATION OF THE CHARACTERIZATION RESULTS OF DIFFERENT ANALYTICAL TECHNIQUES

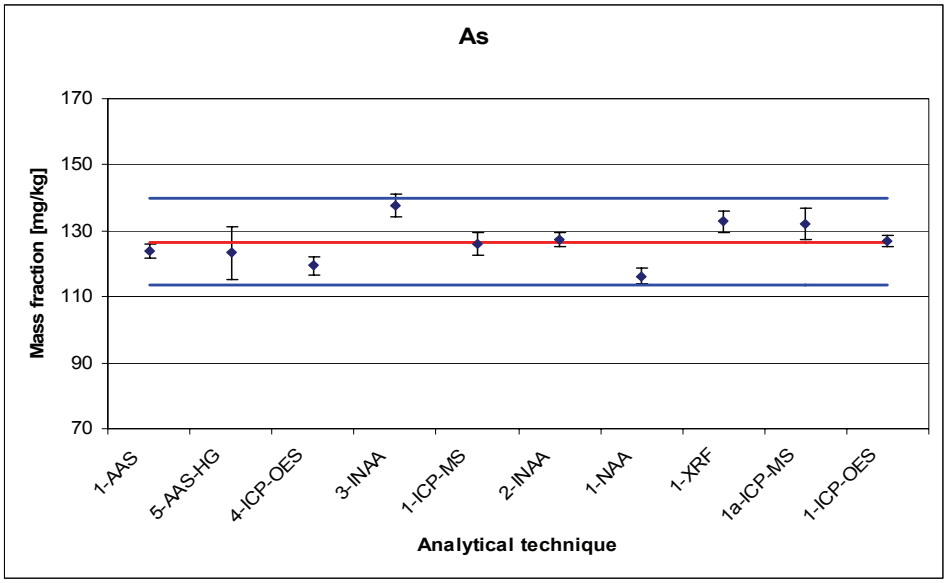
Laboratory means are reported for all techniques and laboratories used for the certification, they are the mean of all individual analysis performed in six bottles and reported with 95% confidence on their standard deviation.

Reference and information values are reported with expanded uncertainty U (k = 2) estimated as a standard deviation of the Mixture Model Median.

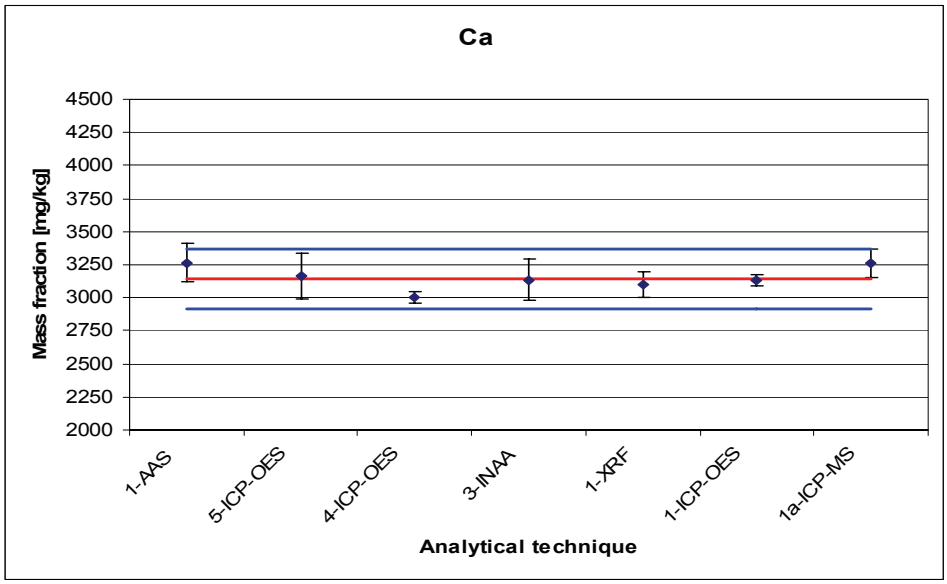
The red line represents the derived property value, the blue lines represent the property value ± U (k = 2).

The information on the x-axis gives the laboratory code and the method used for the characterization. Details on the analysis method can be found in section 5 of the report.

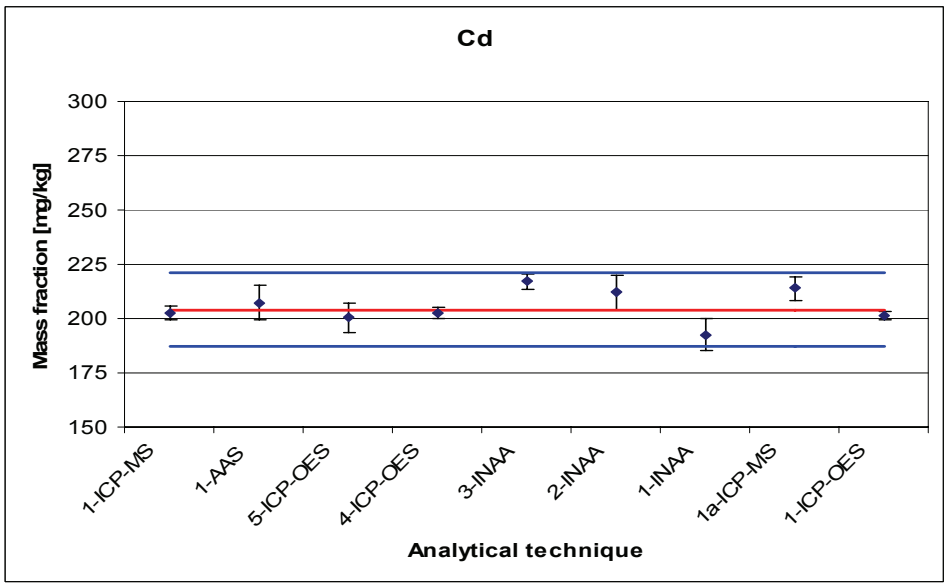
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for As



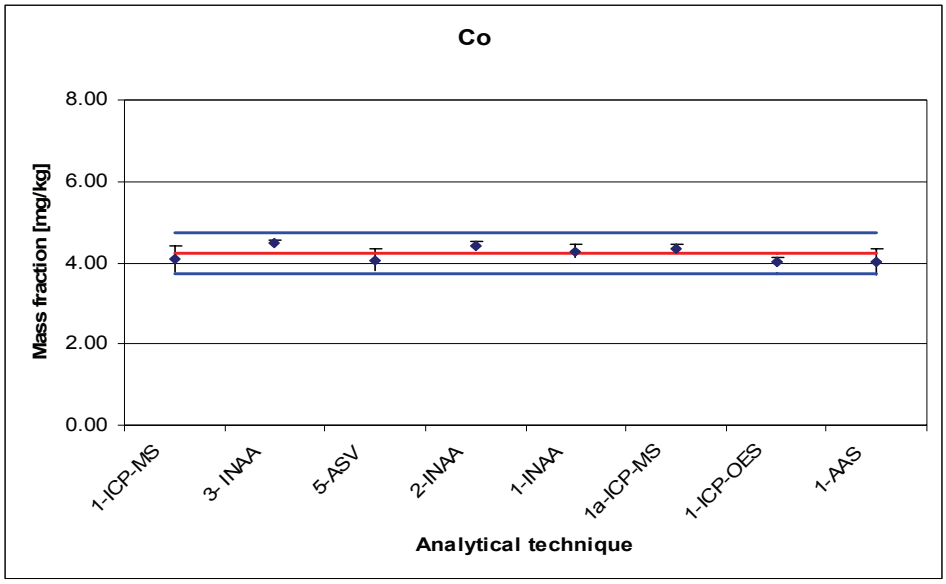
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for Ca



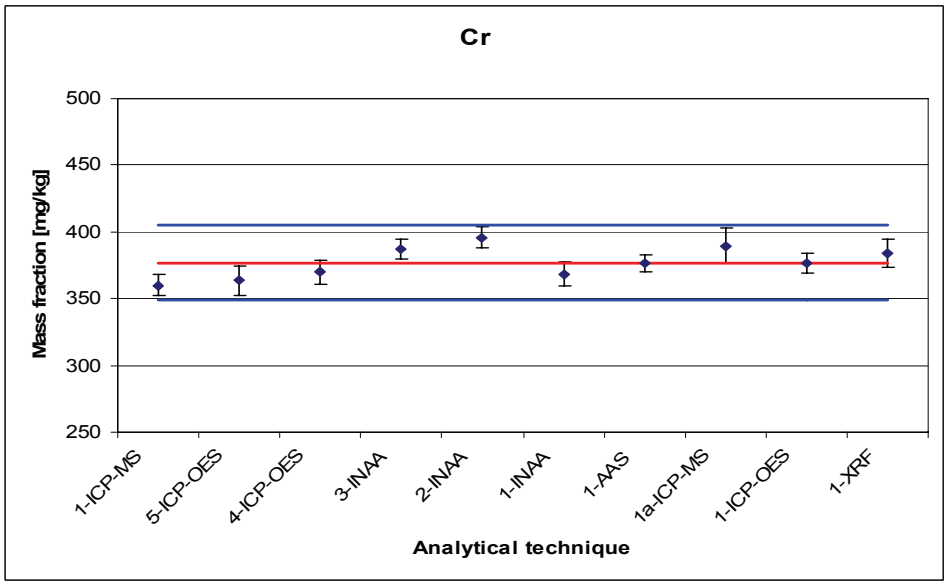
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for Cd



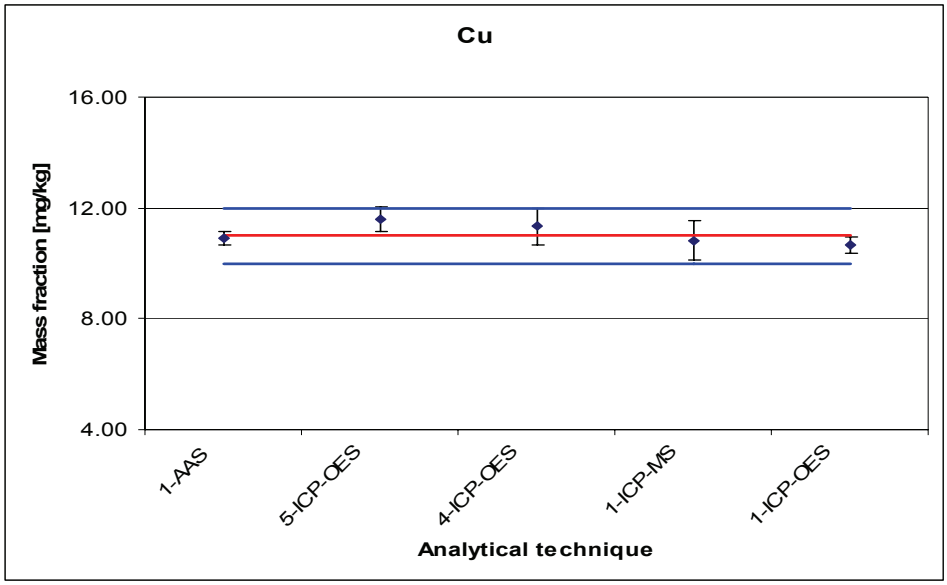
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for Co



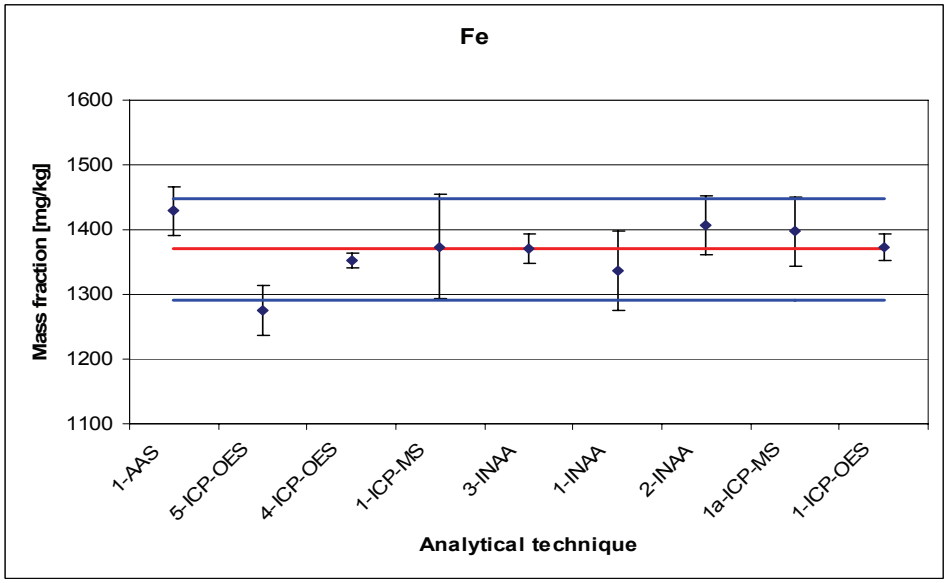
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for Cr



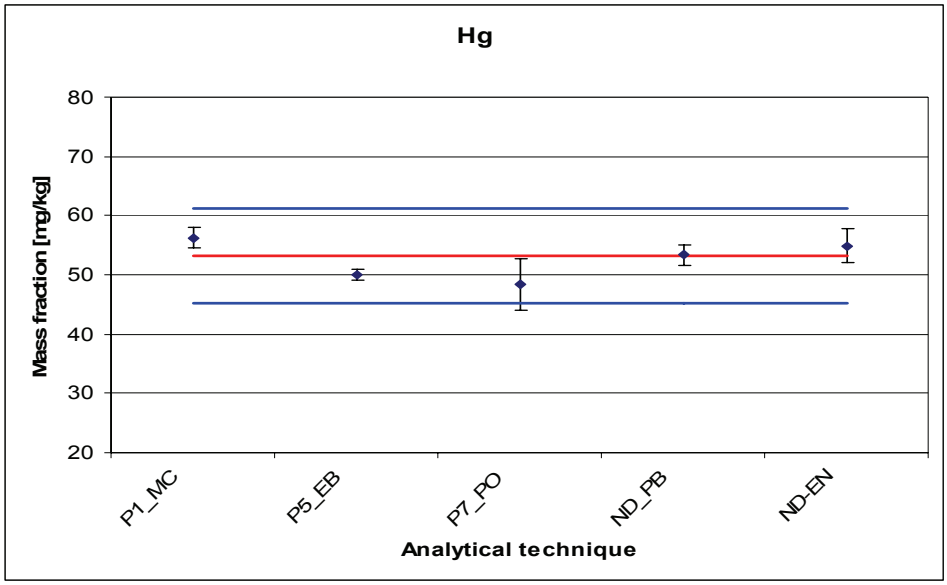
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and information value ± U for Cu



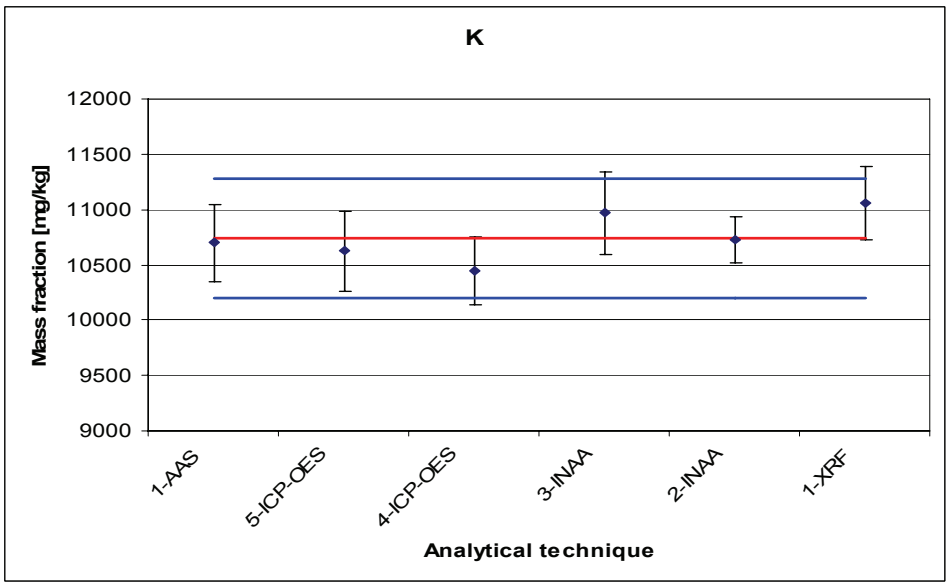
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for Fe



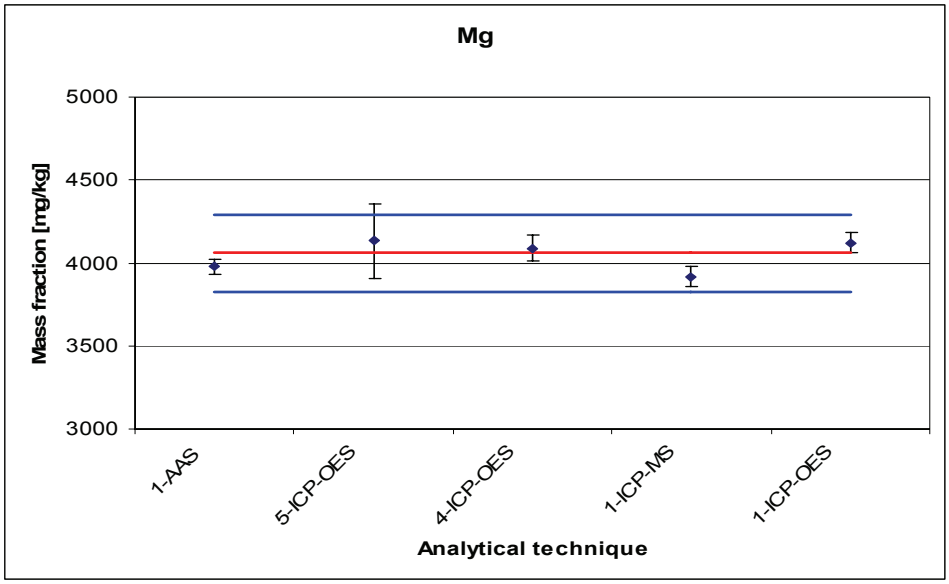
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and information value ± U for Hg



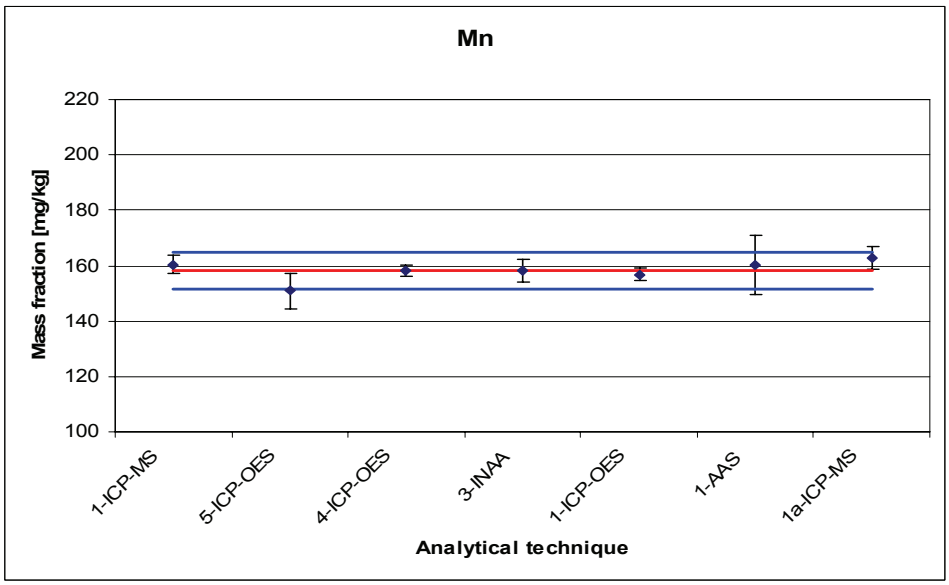
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for K



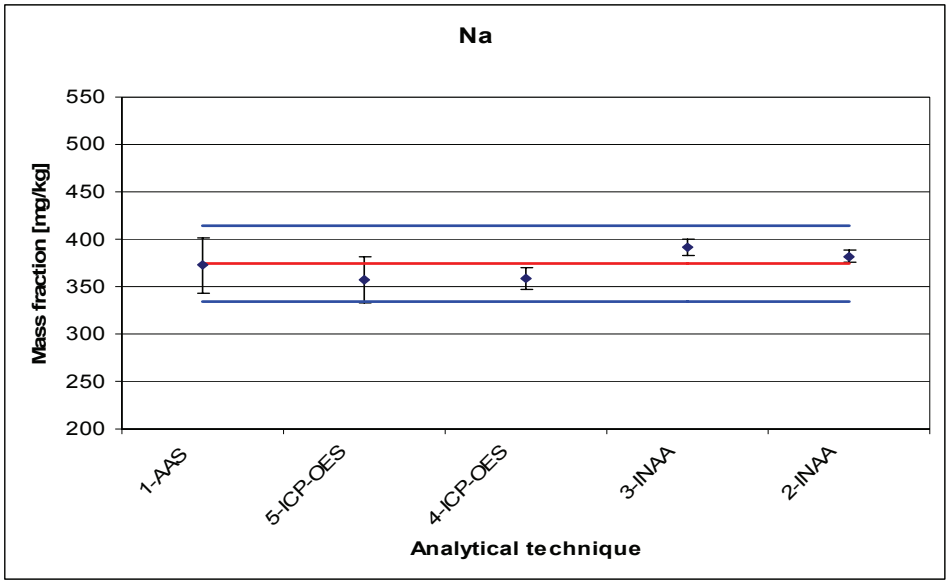
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for Mg



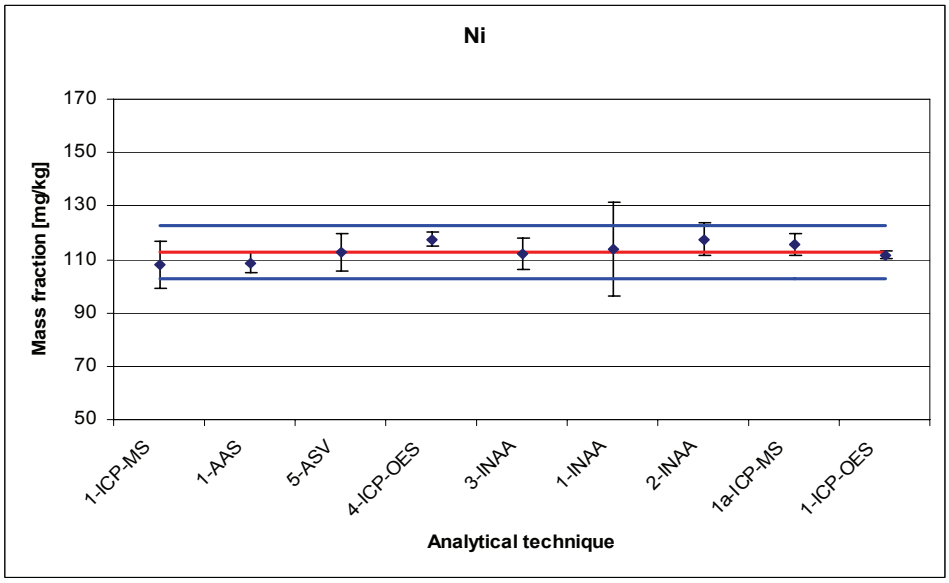
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for Mn



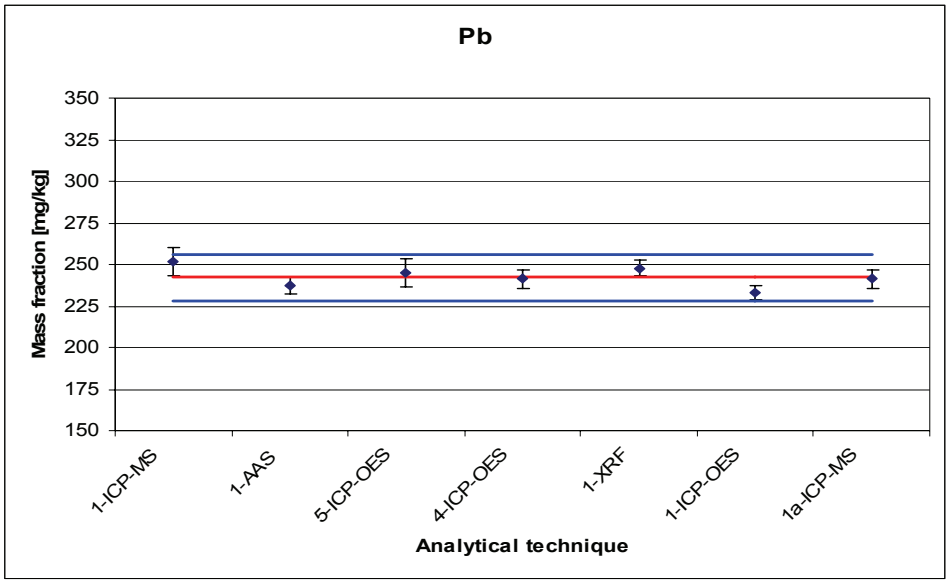
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for Na



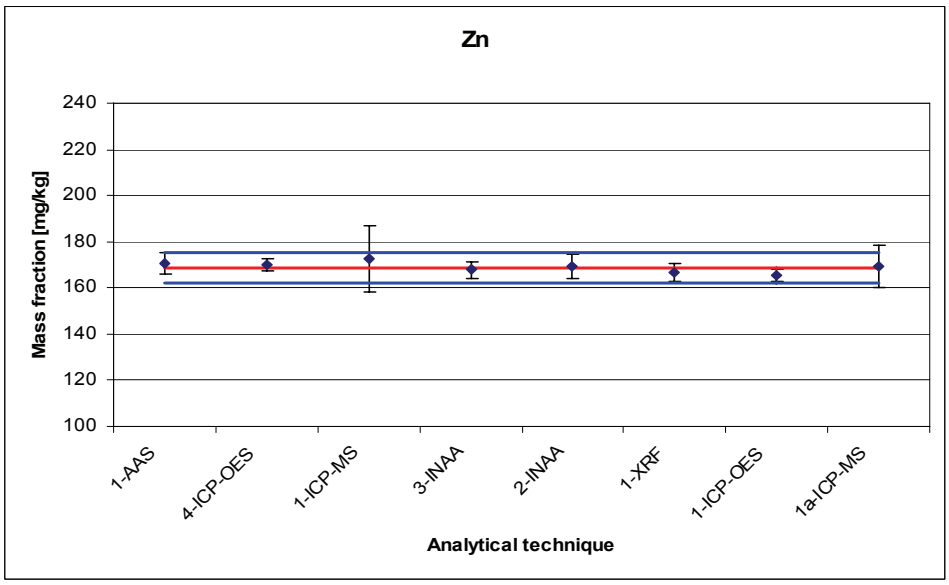
IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for Ni



IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for Pb



IAEA 413, Major, minor and trace elements in Algae
Laboratory means and reference value ± U for Zn



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ABBREVIATIONS

AAS	Atomic absorption spectrometry
ASV	Anodic stripping voltammetry
CV	Cold vapour
ET	Electro thermal
ED-XRF	Energy dispersive X-Ray fluorescence
HG	Hydride generation
HDP	High pressure decomposition
IAEA	International Atomic Energy Agency
ICP-MS	Inductively coupled plasma mass spectrometry
INAA	Instrumental neutron activation analysis
ICP-OES	Inductively coupled plasma optical emission spectrometry
LDP	Low pressure decomposition
ND	Non destructive
PMW	Pressurized microwave
PTFE	Teflon
XRF	X-Ray fluorescence

SAMPLE PREPARATION CODES

ND	Non destructive
P1	PMW, HNO_3
P1HF	PMW, HNO_3, HF
P2	PMW, HNO_3, H_2O_2
P3	PMW, HNO_3, $HClO_4$
P4	open, HNO_3, $HClO_4$
P5	LPD, HNO_3
P6	HPD at 300°C, HNO_3
P7	reflux, HNO_3
P8	PTFE at 180°C, HNO_3

ABBREVIATIONS IN THE EQUATIONS AND TABLES (number of equation and tables in brackets) if not explained in the text

b_1	*Slope* (Table 3)
b_0	*Intercept* (Table 3)
k	Coverage factor (Table 7)
MS_{among}	Mean square (ANOVA) between bottles (2)
MS_{within}	Mean square (ANOVA) within bottles (1, 2, 3)

n	Number of observations (3, Table 3)
n_b	Number of bottles (7, Table2)
n_i	Number of individual measurement results (7, Table 6)
n_L	Number of laboratories participating in the characterization (7,Table 6 and 7)
n_0	(Effective) number of (sub) group members (for complete data sets $n=n_0$) (2, 3)
n_R	Number of replicates per bottle (Table2)
RSD%	Relative standard deviation (Table1)
s	Standard deviation
s_{b1}	Uncertainty of the slope (Table 3)
s_{b0}	Uncertainty of the intercept (Table 3)
s.e.m	Standard error of the mean (Table 2 and 6)
s_i	standard deviation of all individual measurement results (Table 6)
s_{bb}^2	Variance between bottles (2)
S(MM-median)	Standard deviation of Mixture Model Median
s_{bL}^2	Variance between laboratories
s_{wb}^2	Variance within bottles (1)
$u_{\overline{x}}$	Combined standard uncertainty of property value (grand mean) (Table 7)
u_{wb}	Uncertainty related to within bottle variations (Table 7)
u_{bb}	Uncertainty related to between bottle variations (Table 7)
$u*_{bb}$	Uncertainty related to between bottle heterogeneity (3, Table 2)
u_{bL}	Uncertainty related to between laboratory variations (Table 7)
U	Expanded uncertainty (coverage factor 2 for 95% probability) (Table 7)
$\nu_{MS_{within}}$	Degree of freedom of mean square within bottles (3)
x_i	Individual result

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