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INTERCOMPARISON TO IMPROVE THE QUALITY OF TRACE ELEMENT DETERMINATION IN LICHENS

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Analyses of lichens are routinely performed by a number of organizations to monitor the level of atmospheric contamination by toxic elements, e.g. heavy metals. To improve and control the quality of such determinations, the Community Bureau of Reference (BCR) organized an interlaboratory exercise which allowed the detection and removal of most of the pitfalls observed in the determination of a series of 17 elements, namely Al, As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb and Zn. The results obtained in this intercomparison indicated that a certification campaign could possibly be undertaken with some selected laboratories. The materials used in this exercise were collected in Portugal (uncontaminated sample) and Switzerland (contaminated sample). They were prepared carefully and their homogeneity verified. This paper presents the results of the intercomparison.

KEY WORDS: Lichen, trace elements, quality control, intercomparison.

INTRODUCTION

Lichens are currently monitored to aid the control of air pollution and to follow changes in pollution patterns^{1,2}. Lichens are found almost everywhere and accumulate trace elements from the atmosphere; therefore they are often used as a practical means for biomonitoring pollution³. The collection and analysis of lichen material is much easier and cheaper than the use of air-filters; furthermore, the lichen monitoring produces data over wide geographical areas. The quality of lichen analysis is influenced by specific matrix effects which are not matched by the matrix of existing plant reference materials.

About 2000 papers involving lichen analysis have been published in recent years, and reveal high variability of data which may not only reflect different distribution pollution patterns but may also involve analytical errors; furthermore, lichen analyses are often performed for governmental bodies or industries which requires to implement quality control (QC) by demonstrating accurate measurements. A rough estimate has shown that more than

5000 lichen analyses are performed every year within the European Community. This means that consequent economic losses are to be expected if the quality assurance (QA) of measurements performed is not verified.

In order to improve and control the quality of trace element determinations of lichens, the Commission of the European Communities (through the BCR programme) has established a programme the first step of which was intended to detect and remove the main sources of error likely to occur in lichen analysis; the main results of this exercise are presented in this paper along with a description of the programme currently undertaken to produce a certified lichen reference material.

AIM OF THE PROGRAMME

One of the most powerful tools in detecting and removing sources of error due to a particular technique or a lack of QC within a laboratory is to participate in intercomparisons^{3,4,5}. In general, besides the sampling error, the following main sources of error can be identified in all methods for inorganic analyses:

- a) sample pretreatment (e.g. digestion, preconcentration, dilution);
- b) final measurement (e.g. calibration errors, spectral interferences, background corrections);
- c) the laboratory itself (e.g. training and educational level of workers, care applied to the work, clean bench facilities, awareness of pitfalls, management).

When different laboratories participate in an intercomparison, different sample pretreatment methods and different techniques of final determination are compared and discussed as well as the laboratories themselves. If results of such an intercomparison agree, the collaboratively obtained value is likely to be the best approximation of the truth⁶.

An intercomparison can be held to: (i) detect the pitfalls of a commonly applied method and to ascertain its performance in practice, (ii) to measure the quality of a laboratory or a part of a laboratory (e.g. proficiency testing), (iii) to improve the quality of a laboratory in collaborative work in a mutual learning process, and (iv) to certify the contents of a reference material. This paper deals with an intercomparison of (iii) above. The elements considered as a first priority in the intercomparison were: Al, Cd, Co, Cu, Mo, Ni, Pb and Zn and the following elements discussed received less attention: As, Ca, Cr, Fe, Hg, K, Mg, Mn and Na.

PARTICIPATING LABORATORIES

The collection of lichen material was done by the Department of Energy and Botany, University of Lisbon, Portugal (sample TP24) and the Arbeitsgemeinschaft Bioindikation, Berne, Switzerland (sample TP25). The samples were homogenised and bottled at the Joint Research Centre of Ispra (I); homogeneity studies were carried out at the University of Osnabrück (D) and analysed by 32 laboratories all over Europe (see acknowledgements).

PREPARATION

Two samples were prepared for this interlaboratory trial: uncontaminated material (TP24) and a contaminated one (TP25). About 5 kg of TP24 (*Evernia prunastri*) were collected from a "clean" area in Alentejo (Portugal), whereas ca. 500 g of TP25 (*Parmalia sulcata*) was collected from trees growing beside a main motorway in the city of Berne (Switzerland). TP24 was washed to remove dust and/or soil particles whereas TP25 was cleaned without washing, i.e. the coarse particles were eliminated manually.

The materials were dried at 105° C, ground in a titanium mill, sieved and homogenised at the Joint Research Centre of Ispra. The final material consisted of a powder with a maximum particle size of 125 µm; a dark coloured residue remaining on the sieve was discarded. About 200 bottles of TP24 and 60 bottles of TP25 were produced, each containing about 5 g of lichen.

MICROSCOPICAL CHARACTERISATION AND HOMOGENEITY STUDY

As the rejection of the dark residue was questionable in terms of its lichen content, a study using scanning electron microscopy and X-ray scan was carried out on both sieved and residue fractions by Trinity College, Dublin (IRL). The bottled materials were shown to consist of well ground lichen particles with a few larger pieces only. The residue was composed almost entirely of fine much-branched fungal hyphae. The X-ray scan showed that both materials have a rather low heavy element content, the sieved materials containing higher levels than the residues, which was confirmed by INAA determinations performed at the Interlaboratory Reactor Institute of Delft (NL). The residue was predominantly composed of organic material and represented only a small fraction by weight of the whole material (less than 2%); it was therefore considered that the sieved materials were sufficiently representative and suitable for an intercomparison of trace elements i.e. representing the analytical problems usually encountered in lichen analysis (i.e. matrix effects, trace element pattern, major element pattern).

Homogeneity tests were performed by the University of Osnabrück. The elements Cu, Fe, K, Mg, Mn, Pb and Zn were determined by FAAS after digestion of the sample (200 mg) in a closed quartz vessel with HNO₃ at 120° C for 24 h. In most cases the interbottle CV (coefficient of variation), the intrabottle CVs, and the CV of the method (as made up from replicate analyses of a digest solution) were not significantly different. The samples were therefore considered to be sufficiently homogeneous for the interlaboratory trial.

ANALYTICAL TECHNIQUES USED IN THE INTERCOMPARISON

Table 1 summarizes the different techniques of final determination used by these laboratories for the different elements. The pretreatment techniques were digestion with combination of acids in a pressurised or atmospheric mode, programmed dry ashing, combustion, and irradiation with thermal neutrons.

Table 1 Summary of techniques of final determination

<i>Element</i>	<i>Techniques</i>
Al	DCPAES, ETAAS, FAAS, ICPAES, INAA
As	HAAS, ICPAES, ICPMS, INAA
Ca	DCPAES, FAAS, ICPAES, INAA, EDXRF, XRF
Cd	DPASV, ETAAS, ICPAES, ICPMS, IDMS, ZETAAS
Co	DPCSV, ETAAS, ICPAES, ICPMS, INAA
Cr	ICPAES, INAA, ETAAS
Cu	DCPAES, DPASV, ETAAS, FAAS, ICPAES, ICPMS, ZETAAS
Fe	DCPAES, ETAAS, FAAS, ICPAES, INAA, XRF
Hg	CVAAS, INAA
K	FAAS, ICPAES, INAA, XRF
Mg	DCPAES, FAAS, ICPAES
Mn	FAAS, ICPAES, ICPMS, INAA
Mo	ETAAS, ICPAES, ICPMS, INAA
Na	FAAS, ICPAES, INAA
Ni	DCPAES, DPCSV, ETAAS, ICPAES, ICPMS, XRF
Pb	DPASV, ETAAS, FAAS, ICPAES, ICPMS, IDMS, XRF
Zn	DCPAES, DPASV, EDXRF, ETAAS, FAAS, ICPAES, ICPMS, IDMS, INAA
CVAAS	Cold vapour atomic absorption spectrometry
DCPAES	Direct current plasma atomic emission spectrometry
DPASV	Differential pulse anodic stripping voltammetry
DPCSV	Differential pulse cathodic stripping voltammetry
ETAAS	Electrothermal atomic absorption spectrometry
EDXRF	Energy dispersive X ray fluorescence
FAAS	Flame atomic absorption spectrometry
HAAS	Hydride formation atomic absorption spectrometry
ICPAES	Inductively coupled plasma emission spectrometry
ICPMS	Inductively coupled plasma mass spectrometry
IDMS	Isotope dilution mass spectrometry
INAA	Instrumental neutron activation analysis
XRF	X-ray fluorescence
ZETAAS	ETAAS with Zeeman background correction

TECHNICAL DISCUSSION

The results submitted in the intercomparison were discussed amongst all participants at a technical meeting. Each laboratory which participated in the exercise was requested to make a minimum of five independent replicate determinations. The results were presented in the form of bar-graphs showing the laboratory codes and the methods used, the mean and standard deviation of each laboratory and the mean of laboratory means with its standard deviation; the Figure 1 gives an example of bar-graph (copper in TP25 material).

Botanical materials may contain various soil and/or mineral fractions and may therefore be difficult to digest^{7,8}. Poor recoveries of some elements have been observed in certification programmes of plant materials such as white clover⁹ and spruce needles¹⁰. As these materials contain silicates, it is necessary to treat them with HF to ensure complete digestion and total recovery of the metal content. In cases where HF is not used, the laboratory must prove that the residue of the digest does not contain the elements to be determined.

BAR-GRAPHS FOR LABORATORY MEANS AND ST. DEV.

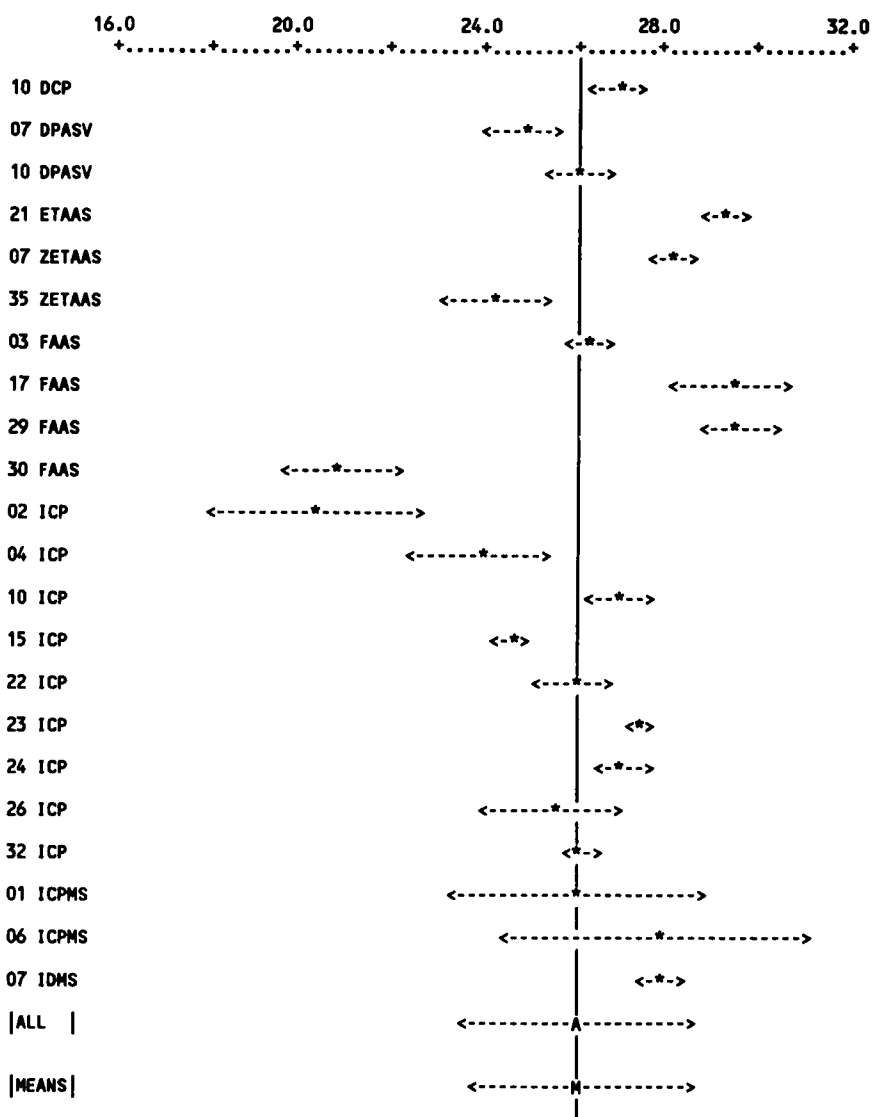


Figure 1 Example of bar-graphs used for the evaluation of the results of the intercomparison (copper in TP25). The laboratory codes are indicated along with the methods used (abbreviations defined in Table 1). The results plotted correspond to five replicate determinations.

Neutron activation analysis is an important method for identifying losses due to incomplete digestion. Care was taken in considering this possible source of error in lichen analysis in the present exercise.

In some cases, sources of errors were demonstrated to be due to contamination, to high dilution factors or to calibration (e.g. for Al, Ca, Cd, Fe, Hg).

Table 2 Summary of the results of the intercomparison. The third column shows the interlaboratory coefficient of variation (CV) prior to the technical evaluation (raw data) and the fourth column lists the CVs after scrutiny of the results (technically accepted values). N is the number of sets of results.

<i>Element</i>	<i>Mean of accepted values (µg/g)</i>	<i>CV% between Labs. (raw data)</i>	<i>N</i>	<i>CV% between Labs. (accepted)</i>	<i>N</i>
TP24					
Al	940 ± 59	28	9	6.3	8
As	0.731 ± 0.096	173	8	13.1	7
Ca	2283 ± 292	28	18	12.8	16
Cd	0.162 ± 0.039	28	18	24.1	16
Co	0.354 ± 0.075	103	14	21.2	11
Cr	1.73 ± 0.33	23	9	19.1	8
Cu	4.80 ± 0.64	27	24	13.3	22
Fe	573 ± 45	134	19	7.9	16
Hg	0.181 ± 0.033	205	8	18.2	6
K	1778 ± 390	43	8	21.9	7
Mg	556 ± 24	8	6	4.3	5
Mn	69.2 ± 3.4	5	13	5	13
Mo	0.219 ± 0.146	142	5	66.7	4
Na	117 ± 29	25	5	25	5
Ni	1.49 ± 0.28	153	20	18.8	14
Pb	5.61 ± 1.11	20	23	20	23
Zn	23.7 ± 3.1	23	27	13.1	26
TP25					
Al	2137 ± 155	13	11	7.3	9
As	0.926 ± 0.121	205	8	13.1	7
Ca	10340 ± 475	25	18	4.6	17
Cd	0.933 ± 0.222	53	20	23.8	19
Co	0.554 ± 0.049	116	14	8.8	11
Cr	9.29 ± 1.34	14	9	14	9
Cu	26.5 ± 3.1	47	29	11.7	25
Fe	1639 ± 258	184	19	15.7	18
Hg	0.252 ± 0.039	164	8	15.5	6
K	6496 ± 500	37	8	7.7	7
Mg	854 ± 36	4	7	4	7
Mn	55.5 ± 3.7	7	14	7	14
Mo	0.835 ± 0.175	73	10	21.0	7
Na	272 ± 259	95	5	95	5
Ni	5.69 ± 1.43	60	21	25.1	19
Pb	145 ± 11	16	27	7.6	23
Zn	147 ± 15	113	29	10.2	25

The results were considered to be acceptable where none of the errors described below could be identified. The Table 2 summarizes the results obtained and shows the interlaboratory coefficient of variation (CV) prior (raw data) and after the technical discussion (accepted values).

Specific remarks were reported for some elements:

Aluminium

The lack of use of a complexing agent (HF, ascorbic acid, oxalate) to keep Al in solution resulted in low (TP24) and very low results (TP25) for some sets of AAS (FAAS and ETAAS) and ICPAES results. Results for Al obtained in the absence of a complexing agent should always be questioned.

Other identified sources of error were contamination and working outside the (linear) calibration range of ETAAS instruments.

The accurate and precise determination of Al by ICPAES requires the measurement of the most sensitive line at 396.152 nm.

Arsenic

A small standard deviation in HAAS was attributed to flow injection which improved the precision. An Fe-interference on the 193.7 nm line of As was observed in ICPAES.

Calcium

Whereas the CV between laboratories indicated a fair agreement for TP25 (4.6%); for TP24, the CV was found to be too high at this level of Ca content (CV of 13.1%). Washing the latter material was suspected of causing stress to the lichen, explaining lower Ca contents and possible poor homogeneities.

Cadmium

The selected data demonstrated a lack of overlap between the results obtained by the different methods, and even between the results obtained by the same method. The lack of overlap was due mainly to the unrealistically small standard deviations. A coefficient of variation $\leq 1\%$ is statistically not realistic when combining digestion and determination processes in the analytical chain.

Cobalt

An accurate determination by ICPAES requires the measurement of non-interfered lines. In this case some of the Co lines were interfered by Fe lines.

A much better agreement was obtained for Co in TP25 (8.8%) in comparison with TP24 (21.2%). This difference could be due to the sample preparation; the washing could have removed a good part of the Co present and therefore the material was no longer representative for the analytical pitfalls involved in lichen analysis.

Copper

Low results were due to an incomplete digestion e.g. by using HNO_3 instead of HClO_4 or HF.

Lead

Most laboratories worked near the detection limits of their methods i.e. below their limit of determination. In some cases, Al-interferences were observed.

The Pb content of TP24 was considered to be too low for a representative material, even for background levels. This is reflected in the difference of CVs observed between the laboratories (19.8 and 7.6% respectively).

Magnesium and manganese

The CV obtained between laboratories showed a high level of agreement (4.3 and 4.2% respectively for Mg, and 4.9 and 6.7% for Mn).

Mercury

Long irradiation in a high neutron flux (INAA) was assumed to cause volatilisation of Hg and therefore to produce low results.

Molybdenum

ICPAES was found to be unsuitable for measuring the 202.03 nm line of Mo.

A high level of disagreement was observed, particularly for the TP24 material (CV of 66.7%); however, the low number of sets of results (4) does not allow firm conclusions to be reached.

Nickel

Contamination problems (by stainless steel) were suspected to be the cause of some discrepancies. The CVs between laboratories (18.8 and 25.1% respectively) are rather high for this level of Ni content and the level of agreement could be improved.

Potassium

As observed for calcium, higher CV between laboratories in the case of TP24 material could

be due to washing effects which induces losses of K. In the case of TP25, the level of agreement of accepted values was found to be fair (7.7%).

Sodium

Very high levels of disagreement were observed, particularly in the case of TP25 (CV of 95.2%). This element was not found to be of great interest for lichen analysis, except for studying marine influences.

FURTHER DEVELOPMENT

This interlaboratory exercise enabled the identification of some sources of error occurring in lichen analysis, which in turn allowed improvement in the state-of-the-art. The results presented in this paper represent a positive illustration of the possibilities of analytical improvements and give a clear example of the need for a good quality control. Based on the results of both the intercomparison and the feasibility of preparation of lichens as candidate reference material(s), a further development of the current project should be designed. The participants agreed that a certification campaign should be contemplated due to the strong need of lichen certified reference materials (CRMs), particularly from polluted environments, for the quality control of trace element analysis. One material was proposed for this purpose (*Pseudevernia furfuracea* growing on pine trees); this lichen material is well suited for monitoring purposes, because it is widely distributed throughout the world. Moreover, it is one of the lichens most often used commercially (e.g. in perfume industry).

For certification, a lichen candidate CRM should be dried at room temperature and all adhering material should be manually removed; It was also shown in the present exercise (material TP24) that the content of some elements, e.g. Co and K, could be affected by washing the material which would then no longer be representative of natural samples and could create additional analytical difficulties; it was assumed that the washing procedure had removed a lot of water-soluble and exchangeable ions such as K which is clearly reflected in the low K contents of TP24. The grinding could be performed under liquid N₂ to avoid contamination with Ti or Al.

This paper is a clear illustration of the effects of intercomparisons on the improvement of the quality of environmental analyses.

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