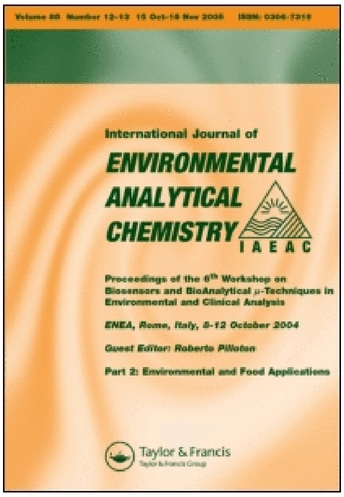

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Some Considerations with Regard to the Quality of Results of Analysis of Trace Element Extractable Contents in Soil and Sediment

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SOME CONSIDERATIONS WITH REGARD TO THE QUALITY OF RESULTS OF ANALYSIS OF TRACE ELEMENT EXTRACTABLE CONTENTS IN SOIL AND SEDIMENT

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Attention is drawn to the necessity to demonstrate accuracy of analytical results in order to make them comparable with results obtained elsewhere in the world. Besides the general aspects of quality management (e.g. within and between laboratories), attention is paid to the pitfalls that may occur in soil and sediment extract analysis. Especially the practical aspects of calibration are being dealt with.

KEY WORDS: Accuracy, analysis, quality control, soil and sediment speciation, calibration.

INTRODUCTION

Measurements are performed to make decisions on the quality of products and goods, to take measures to avoid or to reduce pollution, to better understand environmental processes and so on. The expenditure of developed countries on measurements may amount up to percents of their Gross National Product. The economic losses in case the results are wrong are accordingly high. For example the yearly loss owing to wrong results in the monitoring campaign of the North Sea (appr. 60 laboratories) was estimated at 20 MECU.

In order to improve this situation many laboratories have embarked in quality control programmes. Many studies in which various laboratories analysed the same sample have revealed a large disagreement between their results. Table 1 presents an example recently obtained in the BCR-framework, where approx. 20 laboratories analysed lichen. The results differed so much that any conclusion on possible pollution and pollution sources would have been impossible.

Quality is defined (ISO) as: "the totality of features and characterisation of a product, process or service that bear on its ability to satisfy STATED or IMPLIED needs". In the case of an analytical laboratory where a product (results) is being produced and where the need is to achieve accuracy or comparability of results, we should be able to set up a system

Table 1 Some results obtained in an intercomparison on lichen (BCR 1992).

Element	*Lowest value in µg/g (method)*	*Highest value in µg/g (method)*	*Ratio*
Ca	200 (XRF)	3155(XRF)	15
Cu	0.80 (FAAS)	38.75 (ICP)	48
Hg	0.005 (CVAAS)	0.551 (CVAAS)	110
Mo	0.056(ICPMS)	2.072 (ICP)	37
Zn	9.7 (AAS)	282.5 (ICP)	29

to create this totality of features. Therefore a quality policy (i.e. the overall quality intentions and objectives of an organisation as formally expressed by senior management) can be formulated and a quality control system can be set up. Quality control is then defined as: "the operational techniques and activities that are used to satisfy quality requirements". The EN-45000 series specify to some detail the formal requirements to be posed to a laboratory.

ANALYSIS OF EXTRACTABLE TRACE ELEMENTS IN SOILS AND SEDIMENTS

Within laboratory quality control

The analysis involving extraction schemes consists of three parts:

a. the sample conservation and pretreatment
b. the extraction, following a validated and well-defined scheme
c. the final determination

In this special issue, devoted to sequential extraction schemes, the recommendations deal mainly with the items a and b. This paper therefore gives some general considerations and draws attention to sources of error especially for the case c.

When starting a quality policy a quality assurance manual is to be written which comprises the following items in fair detail:

Test facilities - organisation - personnel
(e.g. safety, location, structure, education, management..)
Quality assessment (e.g. intra- and interlaboratory testings, use of CRM's and RM's..)
Statistical quality control
(e.g. control charts)
Apparatus - chemicals - reagents - blanks
Sampling and storage
Documentation
Reporting of results - archiving

The paper will concentrate on the quality assessment and statistical quality control. These actions are carried out within and between laboratories as presented below:

Quality Control	intralaboratory	Quality control A priori uncertainty estimation - statistical control–control charts CRM's
	interlaboratory	Quality assessment Proficiency testing Method validation

The open literature gives presentations and summaries (e.g. ref 1) which will not be repeated here. The following remarks are therefore not exhaustive but may highlight some of the difficulties.

Sources of errors

Errors may occur in or may originate from:

a) Preparation
- weighing
- making-up of the extraction solutions

b) Extraction
- correction for moisture content
- storage conditions (not-validated)
- absorption/desorption of metals from container surfaces
- contamination (e.g. from reagents or laboratory dust)
- temperature control
- pH control
- losses by precipitation or volatilisation

c) Final determination
- method specific sources of error as summarised in the Tables 3 and 4
- calibration
- insufficient validation

Calibration

The balance should be frequently calibrated as well as all volumetric glassware. The number of laboratories that do not use volumetric glassware in calibration but instead use gravimetric dilution of reagents is rapidly increasing as the advantages in terms of accuracy are well understood.

Table 2 Survey of suitable calibrants.

Element	*Substance recommended*	*Verification*
Al	Al, Al_2O_3	Acidimetric titration or oxydimetric titration e.g. via oxalate
As	As_2O_3	Primary standard of highest purity (sublimation) e.g. available from NIST
Ca	$CaCO_3$	Acidimetric titration
Cd	CdO (subl.), Cd	Chelatometric titration
Cr	$K_2Cr_2O_7$ (dried at 140-150 °C)	Oxydimetric titration
Cu	CuO (heated at 600 °C in air)	Oxydimetric (thiosulphate) or chelatometric titration
Fe	Fe (electrolytical)	Oxydimetric titration
Hg	Hg, HgO	Chelatometric titration
Mn	$KMnO_4$	Oxydimetric titration
Pb	PbO	Oxydimetric titration (via chromate)
Zn	Zn, ZnO	Chelatometric titration

In general and over many years the BCR-experience is that in about 25-30% of all cases eroneous results were attributed to calibration errors. This has also been reflected in the BCR-intercomparison on extractable trace elements in soil and sediment [2] where many laboratories demonstrated to have errors when analysing a common calibrant solution. In fact most discrepancies that occured could be attributed to a biased final determination. This illustrates the importance of calibration. All efforts made to obtain a good sample and perform the extraction under the proper conditions are spoiled if the calibration is wrong.

First of all calibrants should be of good purity and stoichiometry which is to be verified. Compounds containing water of crystallisation should be stored under such conditions that their stoichiometry is maintained. Table 2 summarises some compounds that can be used for calibration together with a verification of their stock solution.

When making a stock calibrant solution preferably two stocks should be made independently, one serving to verify the other; when preparing the dilution (preferably gravimetrically) it is recommended to make two independent solutions again for verification purposes. The alternative would be to verify the new calibrant solution using the previous one.

Calibrant solutions should be made prior to use, even if the solutions are acidified. The laboratory should carefully consider the calibration mode chosen:

i standard additions
ii calibration curve
iii bracketing standards

There is no calibration mode that in all cases should be recommended. All suffer from typical sources of error, e.g.:

i linearity of calibration curve; extrapolation difficulties; chemical form of calibrant added;

ii especially in the non-linear part of a curve, points should be measured often; sometimes even minor changes of the calibrant matrix (e.g. relatively weak complexing agents) change the calibration considerably, which leads to the recommendation to reproduce the matrix in fair detail in matrix-matched solutions

iii bracketing standards in either i or ii mode are an excellent tool to correct for fluctuations in the measurement system; for many routine laboratories, however, they can be very tedious.

The best recommendation to make is probably to validate the methods for each type of soil or sediment type and for the extraction agent applied. Once this is done, the chosen calibration method is more trustworthy.

When diluting acidified calibrant solutions with water hydroxo-complexes can be formed locally (e.g., Al, Ti, Fe..) that only slowly re-dissolve. Therefore dilutions should be made with acid of the same concentration.

Final determination

The techniques applied mostly in this field are: flame atomic absorption spectrometry (FAAS); electrothermal atomic absorption spectrometry (ETAAS) and plasma emission spectrometry (DCP, ICP). The Tables 3 and 4 list some of the critical points that need to be considered in the process of creating a quality system.

All these steps that can cause their particular error have to be examined. Afterwards a control is required using a mimicked analytical solution.

Final remarks

The purpose of this paper has not been to present an extensive survey of analytical problems and of the formalised quality control and assurance as prescribed e.g. in the EN 45000 series. Such survey can be found elsewhere. The purpose has been to draw attention to some of the items stressed in the norms. Experience has shown (cf contribution of A. Ure et al.) that in the group of participating laboratories many laboratories made errors in calibration or in the

Table 3 Typical parameters to be verified in atomic absorption techniques.

Flame gas mixture flow	
Electrothermal	type of tube (graphite, Lvov-platform, wall atomisation ..) matrix modifier injection volume firing programme (drying, ashing, atomisation..)
Background correction	deuterium, Zeeman, Smit-Hieftje, W-iodide
Absorbance	peak height vs area line chosen integration

Table 4 Typical parameters to be verified in plasma emission techniques.

Sample introduction	nebuliser (pneumatic, ultrasonic) wall material (quartz, glass, PTFE)
Spray chamber	type
Sample introduction rate	wall material
Torch	type height
Purge	As, nitrogen, vacuum
Measurement mode	simultaneous vs. sequential
Wavelength used	occasional verification by spectrum scan
Optical resolution	
Integration time	
Background	

setting or selection of experimental and instrumental parameters in the final determination.

It should be stressed in this context that a full implementation of the quality policy rules given in the norms (e.g. 45000 EN) does not implicitly guarantee the absence of error. Implementation of all quality policy is a prerequisite to achieve good results. In addition to a formally laid down quality policy it is necessary to increase the training and motivation of laboratory personel in order to achieve that the policy is carried out in its full extent and with good understanding. Modern personel management techniques with delegation of responsibility and motivation of personel of all ranks, should play an important role.

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