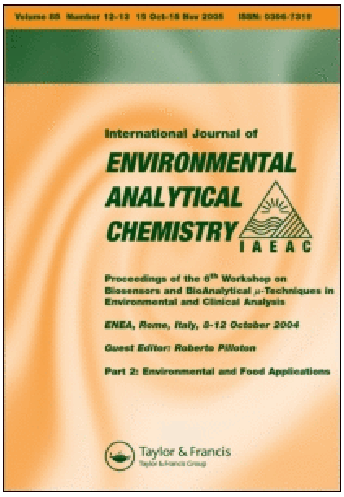

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Improvement of Analytical Measurements within the BCR-Programme: Single and Sequential Extraction Procedures Applied to Soil and Sediment Analysis

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IMPROVEMENT OF ANALYTICAL MEASUREMENTS WITHIN THE BCR-PROGRAMME: SINGLE AND SEQUENTIAL EXTRACTION PROCEDURES APPLIED TO SOIL AND SEDIMENT ANALYSIS

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The determination of extractable trace metal contents in soil and sediment, using respectively single and sequential extraction procedures, is currently performed in many laboratories to assess the bioavailable metal fraction (and related phyto-toxic effects) and the accessability to the environment (e.g. contamination of ground waters).

Owing to the need for validation of the extraction schemes used and of the analytical techniques, the Community Bureau of Reference (BCR) decided to organize a project for the improvement of the quality of determinations of extractable trace metal contents in soil and sediment. The implementation of this project follows a stepwise approach involving feasibility studies, intercomparisons to detect and remove sources of errors in the application of the analytical methods, and the certification of the extractable compounds. This paper describes the organization of the work completed so far (feasibility studies and first intercomparison) and discusses its further development.

KEY WORDS: BCR-aims, intercomparison, certification, single extraction, sequential extraction, validation.

INTRODUCTION

The eco-toxicity and mobility of metals in the environment depends strongly on their specific chemical forms or method of binding rather than the total element contents. Consequently these have to be determined in order to assess the toxic effects and geochemical pathways. The determination of specific chemical species or binding forms is difficult and often hardly possible. Therefore, in practice determination of broader forms or phases defined by their function can be a reasonable compromise; e.g. "bioavailable" forms of trace elements can give sufficient information to arrive at a sound environmental policy. The increasing concern to assess the bioavailable metal fraction (and thus to estimate the related phyto-toxic effects) and the environmentally accessible trace metals upon disposal of e.g. sediment on to a soil (e.g. contamination of ground waters) is reflected by a considerable increase in the frequency of analysis over the last ten years. Single and sequential extraction schemes have been designed in the 80's in order to assess the different binding forms of metals in soil and sediment samples [1,2,3,4,5]. However, the lack of uniformity in the different procedures used did not allow the results to be compared worldwide or the procedures to be validated; this led to critical comments from many scientists [6,7]. Indeed, the results obtained are "operationally defined" [1], i.e. the "forms" of metals are defined by the determination of extractable elements using a given procedure, therefore the significance of the analytical results is highly dependent on the extraction procedures used. This type of determinations are often referred to as "speciation" although this term strictly speaking cannot be applied to operationally defined procedures (speciation comprises rather the determination of specific form, e.g. oxidation state or organometallic compound, in which an element can occur).

Moreover, the lack of suitable reference materials for speciation studies did not enable the quality of the measurements to be controlled. The aspect of quality control and different sources of error likely to occur in inorganic analyses is further discussed by Griepink in this issue [8].

Because of the likelihood of the many sources of pitfalls which may occur, the Commission of the European Communities through its BCR-programme (Community Bureau of Reference) has implemented a project for the improvement and harmonization of measurements for extractable trace metal contents in soil and sediment. This followed a stepwise approach (feasibility, intercomparisons, certification) of which the aims are described in this paper.

AIM OF THE BCR-PROGRAMME AND APPROACH

The BCR-programme is a Research and Development programme of the Commission of the European Communities whose objective is to improve the quality of measurements and consequently harmonize the results of the measurements obtained within the European Community. This task essentially consists of organizing projects in which participating laboratories may collaborate to improve the measurement or analysis concerned. The implementation of projects usually follows a stepwise approach of several phases e.g.:

- Feasibility study
- Intercomparisons (step by step approach)
- Certification

Feasibility study

Where difficult analytical or preparatory problems are faced, small scale feasibility studies are often conducted prior to organizing a larger project. These may address the improvement of stability of analyte and matrix, the development of analytical methods or chemical treatment procedures and the validation of method as used.

Owing to the need for establishing a common scheme for single and sequential extraction, as discussed by Muntau [9], a feasibility study was organised aiming at comparing four different schemes. The details of this study are described by Ure *et al.* [10] in this issue and discussed in an extensive report [11]. The main conclusions were that a reasonable agreement could be found with the different procedures (i.e. similar general conclusions could be drawn regarding e.g. the mobility of trace metals) but that the comparison of the data was difficult in many cases. This feasibility study demonstrated clearly that broadly accepted extraction schemes should be established; a discussion amongst European experts thus led to the design of a protocol to be used in a first intercomparison of soil (EDTA, acetic acid and ammonium acetate single extraction) and sediment (sequential extraction involving acetic acid, hydroxylammonium chloride, ammonium acetate and hydrogen peroxide).

Further to the first intercomparison described below, another feasibility was conducted on the improvement of an ammonium acetate extraction to be used in a second exercise; the results of this study are summarized in this issue [12].

Step by step approach

General The analytical methods used for the determination of chemical forms of elements are based on successive steps e.g. extraction and detection which should be examined separately to verify the laboratory's performance and evaluate the sources of error which might arise.

The evaluation of sources of error may be done by using samples previously characterised for their homogeneity and stability which are distributed to the participating laboratories. Typical matrices are e.g. solutions containing the analytes of interest to evaluate the performance of the final detection and real samples to test the total analytical procedure (extraction and detection). In the case where a separation step is involved, cleaned extracts may be used to test its performance.

The different steps enable the sources of error to be identified and consequently help the laboratories to remove them. The results of the exercises are discussed in technical meetings with all the participating laboratories who may share their experience. Such intercomparisons may also enable the detection and removal of any bias linked to a particular method or a particular laboratory. Systematic errors in the measurement such as contamination, losses, calibration error etc. Can be identified by comparing different detection procedures.

Application to soil and sediment speciation analysis With regard to the determination of extractable contents of trace metals in soils and sediments, a first intercomparison has been successfully concluded [11]. This exercise involved the analysis of calibrant solutions of the elements of interest (Cd, Cr, Cu, Ni, Pb and Zn), the determination of their EDTA, acetic acid and ammonium acetate extractable contents in a sewage sludge amended soil, and the use of a sequential extraction procedure (mentioned above) for the determination of extractable trace metal contents in a marine sediment sample.

35 European laboratories (listed in the Annex) participated in this exercise which enabled the sources of error in the analytical methods to be detected. Moreover, the extraction protocols used in the intercomparison were amended by the experts in order to design a common procedure [11] which would lead to a European standard.

The results of soil analysis were promising enough to encourage the BCR to organise a certification campaign as described below. However, for a sequential scheme as applied to sediments, a second intercomparison using a redefined protocol was found to be necessary; this exercise is currently being carried out using a river sediment.

Certification

General The certification of reference materials (CRMs) is carried out only if the intercomparisons have demonstrated that the participating laboratories have identified and removed all the systematic errors from their procedure(s) i.e. the results of various methods are in good agreement.

The CRMs produced are as close as possible to real matrices to mimic the analytical difficulties encountered in the analyses of environmental samples; they are made available by the Commission of the European Communities along with a certification report describing their preparation, the homogeneity and stability studies, the analytical methods used and the certified values.

A CRM can thus be considered as a material which disseminates the experience collected by those laboratories who improved the quality of their measurements in intercomparisons and demonstrated their accuracy [13].

Certification of extractable trace metal contents in soil On the basis of the results of the first intercomparison [11], a project has started for the certification of extractable trace metal contents in soil using two single extraction procedures (EDTA and acetic acid) which are described in detail in this issue [10]. Two soils were collected for this purpose, i.e. a sewage sludge amended soil originating from England and a terra rossa soil collected near Barcelona.

The homogeneity and stability of the EDTA and extractable trace metal contents will be verified and the samples will be distributed to the participants for analysis. It is expected that these two soils could be certified in 1993.

CONCLUSIONS

The BCR-programme aims at improving the quality of measurements and harmonizing the results obtained within the European Community. This goal is achieved by organizing collaborative projects in which laboratories may validate their analytical procedures. In certain cases, the adoption of a common procedure may be decided to enable a comparison of data obtained throughout the Community, e.g. common extraction procedures (single extraction for soil and sequential extraction for sediment) have been adopted by ca. 40 European laboratories for the certification of extractable trace metal contents in soil and sediment. It is hoped that these schemes could attribute to the development of an international norm (e.g. ISO, CEN) which would allow for a worldwide comparison of the results obtained.

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ANNEX

ADAS/MAFF, Government Offices, Wolverhampton	UK
Agriculture and Food Development Authority, Wexford	IRL
Agricultural Research Centre, Inst. for Crops and Soil, Jokioinen	SF
Bund. für Materialforschung und Prüfung, Berlin	D
CEC, Joint Research Centre, Ispra	I
Chalmers Univ. of Technology, Göteborg	S
Environmental Pollution Control Laboratory, Thessaloniki	GR
Estação Agronomica Nacional, Dept. de Pedologia, Oeiras	P
Estación Experimental del Zaidin, C.S.I.C., Granada	E
Federal Research Centre of Agriculture, Braunschweig-Volkenrode	D
Istituto Chimica del Terreno, Pisa	I
Istituto di Chimica Agraria, Bari	I
Institut für Wasser, Boden und Lufthygiene, Berlin	D
Institut de Géologie du Bassin d'Aquitaine, Univ. de Bordeaux I, Talence	F
Institut National d' Agronomie, Laboratoire de Chimie Analytique, Paris	F
Institut National de Recherche Agronomique, Villenave d'Ornon	F
Institut National de Recherche Agronomique, Lab. d'Analyse des Sols, Arras	F
Institut for Soil Fertility, Haren	NL
Kemtiteknik, Teknologisk Institut, Taastrup	DK
Laboratoire Central des Ponts et Chaussées, Bouguenais	F
Laboratory of the Government Chemist, Teddington	UK
Landbouw Univ., Wageningen	NL
Leiter Labor, Arbeit- und Umweltschutz, Nordenham	D
Nova Universidade de Lisboa, Monte da Caparica	P
Rijksuniversiteit Gent, Lab. of Analytical and Agro-Chemistry, Gent	B
Rothamsted Experimental Station, Herts	UK
Severn-Trent Laboratories, Coventry	UK
Station Fédérale de Recherches en Chimie Agricole, Liebefeld-Bern	CH
Technische Universtität, Arbeitsbereich Umweltschultz-technik, Hamburg	D
The Macauley Land Use Research Institut, Aberdeen	UK
Universidad de Barcelona, Dept. de Química Analítica, Barcelona	E
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Water Research Centre Medmenham, Buckingham	UK