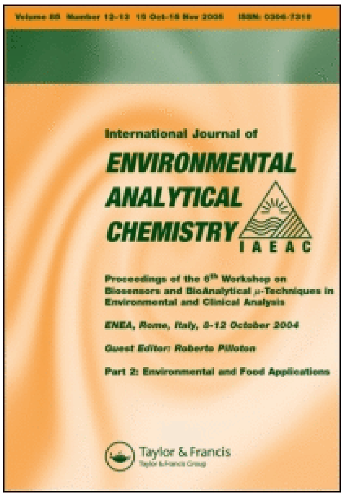

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CONCLUSIONS OF THE WORKSHOP

SINGLE AND SEQUENTIAL EXTRACTION IN SEDIMENTS AND SOILS

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The determination of extractable trace metal contents in soils and sediments is currently performed in many laboratories to assess the bioavailable metal fraction (and related potential phyto-toxic effects) and the importance and possibility of mobilization of trace metals from polluted soil, sludge and sediment upon landfill application. Single and sequential extraction schemes are used for the assessment of the different "forms" of trace metals (e.g. "mobile/bioavailable", "carbonate-bound" etc.). The lack of uniformity in the different extraction procedures used throughout the world does not allow the results to be compared or the procedures to be validated which has led to many criticisms in the past few years. Moreover, the lack of suitable reference materials for this type of operationally defined determinations did not enable the quality of the measurements to be controlled. Owing to the need for establishing common schemes for single and sequential extractions as well as for the improvement of the quality of extractable trace metal determinations in soil and sediments, the Community Bureau of Reference (BCR) has organised a project which results along with the state of the art of extractable trace metal determinations, use and applicability of extraction schemes and analytical limitations were decided to be thoroughly discussed in a workshop. This paper presents its main conclusions.

KEY WORDS: Single and sequential extraction, application, state of the art, analytical limitations, common scheme, quality control.

INTRODUCTION

The determination of extractable trace metal contents in soils and sediments is currently performed in many laboratories to assess the bioavailable metal fraction (and related potential phyto-toxic effects) and the importance and possibility of mobilization of trace metals from polluted soil, sludge or sediment upon landfill application. Single and sequential extraction schemes are used for the assessment of the different "forms" of trace metals often defined as e.g. "mobile/bioavailable", "carbonate-bound", "residual" etc. The term "speciation" is generally used although the group determinations being operationally defined, this wording strictly speaking cannot be applied. The lack of uniformity in the different extraction procedures used does not allow the results to be compared worldwide or the procedures to be validated which has led to many criticisms in the past few years. Indeed, the results obtained are highly dependent on the extraction procedures used. Moreover, the lack of suitable reference materials for this type of analysis did not enable the quality of the measurements to be controlled. Owing to the need for establishing common schemes for single and sequential extractions as well as for the improvement of the quality of extractable trace metal determinations in soil and sediment, the Community Bureau of Reference (BCR) has organised a project of which the first step was to identify the most frequently used procedures upon consultation with European experts and to test these procedures in interlaboratory exercises.

At this stage, having conducted 2–3 intercomparisons, it was found highly necessary to discuss the results obtained thoroughly and a workshop was therefore held for this purpose; all the participants in the project were invited. The aim of the workshop was to establish the state of the art of extractable trace metal determinations, to define the use, applicability and necessity of the determination of forms of metals, to investigate where limitations exist and discuss the work necessary to overcome these as well as the identified sources of error.

SUMMARY OF ROUND-TABLE DISCUSSIONS

Sampling

The sampler should consist of materials, such that no contamination by the elements sought for could occur. For soil, the use of carbon steel sampler and the removal of oxidation products (rost) prior to use were recommended.

Handling operations were found to be a critical step for the preservation of the speciation, e.g. sediments are critical with respect to oxygen. Therefore, unavoidable operations to be carried out in the field were recommended to be performed in an inert gas-filled glovebox or glovebag, operated with continuous gas-purging. Top soils are typically oxygenated to some extent and for them such handling procedures are, therefore, not mandatory.

In the case of storage, no agreement was considered to be possible for achieving the best conservation after collection if immediate analysis, which is most appropriate, was not possible. However, it was agreed that the risk of errors owing to irreversible changes of the matrix increases in the following order:

(i) conservation by rapid freezing and storage in liquid nitrogen (shock freezing);
(ii) conservation by storage in ice (0–5°C);
(iii) drying.

For sediments, core sectioning must be done prior to transport.

If drying was chosen as a means to preserve the sample's integrity, the ISO draft for drying soil samples was recommended (i.e. drying of e.g. 0.5 kg of soil in air at less than 40°C); the aggregates should be broken down, not ground. The instantaneous extraction properties can only be determined immediately after sampling or after a few days on samples stored at 0–5°C.

In the case of sediments, it was recommended that the extraction procedure be applied to the wet, homogenized and sieved (2 mm) sediment without drying; sieving, homogenization, sub-sampling and weighing should be done in an inert gas-flushed glovebox.

The critical holding time was considered to range from days to hours in case of reactive sediment samples, and for days in the case of soils.

Specific remarks were made for the possible preparation of candidate reference materials (RMs) of soil and sediment: oxic sediment samples could be stabilized upon drying for use as a RM. However, anoxic samples can only be handled in inert atmosphere in a glove box; the sampling, handling and stabilization of anoxic sediments are recognized to be very critical and should be investigated further. In addition, the particle size distribution should be studied and given for a candidate certified RM.

In the case of soil, the participants mentioned that there is a need for a CRM of calcareous soil. For sediment, a first choice for a CRM was oxic lake or river sediment; marine samples were not recommended.

Practical experience with reagents and matrices

Centrifugation after extraction is preferred to filtration; if filtration is used it should be done immediately after extraction to avoid readsorption (due to an extension of the leaching time). After centrifugation, it is essential to separate the solid residue completely. The two protocols (single extraction for soil and sequential extraction for sediment) were thoroughly discussed during this round-table and were amended; the final version of the procedures are given in this issue [1]. Weaker extractants (e.g. ammonium nitrate, calcium chloride …) were also proposed for consideration in a later stage of the project.

Some technical remarks were made for both soil and sediment analyses e.g. horizontal shaking was the preferred method of the participants; for sediment, decantation was preferred to pipetting, the overnight shaking should be carried out at constant temperature (20 ± 2°C) and the pH of the final solution should be measured and brought to pH 4 with acetic acid. The sediment should be resuspended between each extraction step (e.g. breaking of the "cake" obtained upon centrifugation by using a fast rotating plate between each step). Finally precautions should be taken to avoid violent reaction with reagent C (see protocol in ref. [1]) when the sediment is transferred to the beaker.

As a conclusion it was stressed again that the aim of use of extraction protocols is to define the operational procedures (e.g. EDTA extractable …) and not the "species".

Analytical problems after extraction

Some analytical problems after extraction may be due e.g. to incomplete separation of the solid residue after centrifugation or readsorption if filtration is used as mentioned in the previous paragraph. It was outlined that a complete separation of the residue was essential; in addition it was repeated that centrifugation should be used instead of filtration.

The extracts should be analysed immediately after separation; in case this would not be possible then storage at 4°C for a maximum of 24 hours was considered to be acceptable to preserve the sample integrity.

In step 3 of the sequential extraction, residual H_2O_2 may interfere in blank determinations and can be destroyed by UV irradiation or by addition of ascorbic acid.

Owing to the expected interferences in FAAS and ICPAES, it was recommended to perform a calibration using standards matched to the extractant matrix; a calibration curve based on matrix matched calibrant solutions was preferred to standard additions; such curve should comprise the actual point measured (i.e. made up from measurements on calibrant solutions having a lower and a higher concentration than the unknown). For ETAAS, calibration should be by standard additions, in the linear region of the calibration curve, to compensate for matrix interferences and differences in actual temperature programme; background reduction by use of modifiers or Zeeman background correction can be used as well as destruction of colloids by addition of aqua regia and microwave heating. Dilution, if required, should be made with the extractant. It was agreed that the use of signal peak area for quantification is more reliable than peak height.

Ammonium acetate extraction, justification and precautions for use

The participants did not consider that ammonium acetate had sufficient merit to be recommended as a third extractant (in addition to the extractants used in the intercomparisons namely EDTA and acetic acid) as its correlation with plant uptake is relatively poor; moreover, ammonium acetate is not very useful for calcareous soils. Finally, additional analytical problems may occur owing to the very low trace metal contents extracted by ammonium acetate and due to the high blanks present in the reagents. However, ammonium acetate extraction may be a useful tool for studying the potential mobilization of heavy metals associated to suspended particulate matter in water and soil solutions; for this purpose, ammonium acetate 1 mol/l at pH 7 was recommended. The validation of use of the weak extractants such as ammonium acetate was considered to be necessary and further investigations were encouraged.

CONCLUSIONS

The outcome of the workshop presented in this paper will benefit for the scientific community for several reasons. First, the open discussions of specific topics enabled both the creation of a collaborative atmosphere which is necessary for bringing a stone to the European construction and for considerable improvement of the understanding of extraction procedures applied to soil and sediment samples. The recommendations issued from the round-table discussions and plenary sessions and which are implemented in the standard operating procedures for extraction [1] showed that the adoption of common schemes could attribute to the development of an international norm (e.g. ISO, CEN) which hence would allow for a worldwide comparison of the results obtained. The participants of this workshop were all convinced that this development would give a new start in the use of extraction procedures for environmental studies.

It is expected that the harmonization gained by the use of common schemes, supported by the availability of reference materials certified for their trace metal extractable contents, will allow for a comparison of the data produced within the European Communities and hence for mapping and modelling purposes.

The conclusions of the workshop described in this paper have been agreed among all the participants who belong to the leading European laboratories in this field.

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