

Chemicals Regulation

Harmonisation, Standardisation for Soil and Sediment Fractionation Studies, and Usefulness in Assessment and Risk Management

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DOI: <http://dx.doi.org/10.1065/jss2001.09.024>

Abstract. Single and sequential extraction procedures are often used to study the environmental fate of trace elements from soils and sediments. Although these schemes are quite popular, they are prone to various sources of errors, which require them to be thoroughly controlled. Owing to their operationally-defined character, the only way to compare analytical data is to stick closely to procedures that have been collaboratively studied and written in the form of an operating protocol. Groups of scientists have hence developed 'harmonised' procedures that are used as a reference for fractionation studies. A higher level is the formal standardisation of the procedures by official standardisation bodies, which also fulfils the need for achieving the comparability of data obtained by different laboratories from different countries. This paper discusses aspects of harmonisation (consensus obtained by groups of scientists) and standardisation (adoption of standards as mandated by an international organisation) as applied to single and extraction schemes for trace element fractionation studies, including quality control aspects.

Keywords: Extraction, single and sequential; fractionation studies; harmonisation; interlaboratory studies; phosphate; quality control; reference materials, certified; sediments; soils; standardisation; trace metals

ganometallic compounds) is often difficult in soil and sediment matrices and, to date, only very few compounds have been reported to be accurately determined in sediment (e.g. tributyltin, methyl-mercury) using e.g. hyphenated techniques involving a succession of analytical steps (extraction, separation, detection). In practice, environmental studies on soil and sediment analysis are often based on the use of leaching or extraction procedures (e.g. single or sequential extraction procedures), enabling broader forms or phases to be measured (e.g. 'bioavailable' forms of elements), which are in most instances sufficient for the purpose of environmental policy (Quevauviller 1998). However, the lack of uniformity in the procedures used did not allow the results to be compared worldwide nor the methods to be validated. Indeed, the results obtained are 'operationally-defined' which means that the 'forms' of elements are defined by the determination of extractable fractions, using a given procedure and that, therefore, the significance of the analytical results is highly dependent on the extraction procedures used. This type of determinations is often referred to as 'speciation' although, strictly speaking and according to the recent IUPAC definition of 'speciation' (Templeton et al. 2000), this term should not be applied to operationally-defined procedures. Speciation would cover the determination of well-defined chemical species (e.g. organometallic compounds, metals with different oxidation states, etc.), whereas the extracted 'forms' should be only related to the extractant used, e.g. EDTA-extractable element, and not as e.g. 'bioavailable', 'mobile', etc. forms, which are rather interpretations of data than results of actual measurements. This type of measurement is also referred to as 'fractionation'. Results are useful and usable only if they correspond to well-defined and accepted procedures. In other words, the only mean for achieving a sound interpretation and basis for decisions is to achieve the comparability of results, which is closely linked to a consensus with respect to the used procedures, followed by their validation, and their possible implementation as a standard.

This paper discusses the aspects of 'harmonisation' versus 'standardisation' of single and sequential extraction schemes. In particular the approach followed by the Standards, Measurements and Testing programme (formerly BCR) for harmonising single and sequential extraction procedures for soil and analyses is described, the final aim of which was to provide laboratories with reference schemes to achieve comparability of data related to extractable trace metals and phosphate contents. Details on the different selected and tested schemes, namely EDTA, DTPA, and acetic acid for extractable trace metals in soils, three-step sequential extraction

Introduction

The use of single and sequential extraction schemes for soil and sediment analysis is not what we could call a new feature. The development and use of extraction schemes for trace element fractionation studies have started at the end of the 70's (Tessier et al. 1979, Meguelatti et al. 1983, Förstner 1983, Salomons and Förstner 1984), and aimed to evaluate the metal fractions available to plants (and thus estimate the related phyto-toxic effects) and the environmentally accessible trace metals (e.g. mobility of metals from a soil and potential groundwater contamination). These schemes have been adapted and are still widely used for soil and sediment studies as reflected by the number of recently published papers dealing with the applications of these procedures (McGrath 1996, Gupta et al. 1996, Marin et al. 1997, Mester et al. 1998). Their use relies on the knowledge that the environmental eco-toxicity and mobility of environmental contaminants is strongly dependent upon their specific chemical forms or way of binding, i.e. toxic effects and biogeochemical pathways can only be studied on the basis of the determination of these 'forms' or 'fractions'. The determination of chemical species of elements (e.g. or-

scheme for extractable trace metals in sediment analysis, and sequential extraction scheme for extractable phosphate in sediment, are given in the literature (Quevauviller 2001) and will not be repeated here. As discussed later, the collaborative testing of these schemes, along with the preparation of related Certified Reference Materials (CRMs), has a clear effect on their worldwide use which is increasingly reflected by the literature. The schemes are not standardised *sensu stricto* (i.e. they were not adopted as official standards by an international standardisation organisation), but they fulfil the same role in enabling data comparability in this analytical field. The paper discusses the meaning and implication of a 'harmonised' and 'standardised' scheme with some critical comments on the latter. These considerations are extracted from a book that gives an overview of extraction procedures currently used for soil and sediment analysis (Quevauviller 2001). Many of these schemes are currently used for risk management studies, in particular for soil remediation and contamination studies.

1 Standardisation

One of the principles of standardisation is to 'write what is done' and to 'do what is written'. A standard may be defined as a reference text, which has been elaborated by a recognised – national or international – organisation (e.g. AENOR in Spain, AFNOR in France, DIN in Germany, BS in the United Kingdom, etc., CEN for the European Union, and ISO at the world scale) after agreement of all interested parties. Fig. 1 recalls the process of preparation of a standard (Lombard 1999). It should be noted that the adoption and implementation of a standard corresponds to a formal action that is either mandated by a regulatory body (e.g. the European Commission) or international organisations (e.g. Trade or Industry associations).

With respect to analytical science, many discussions have arisen on the risks that standardisation might 'fossilise' progress in a wide range of cases. This may be true for analytical methods that may evolve with technological progress and that would soon become outdated if they would be standardised without any possibilities to improve them. One should realise, however, that the adoption of 'standardised' procedures is the only way to achieve comparability when using operationally-defined procedures. In other words, the strict application of written protocols is mandatory in such cases to achieve data comparability. This does not infer that improvements should not be investigated to ensure progress in the use and result interpretation of these schemes; in this case standardisation actually offers scientists a possibility to speak the same language and decision-makers a way to identify better possible strategies for environmental risk assessment. Extraction tests are widely used for the assessment of the release of inorganic contaminants from soils, sludges and sediments. In many instances, these schemes are included in national (or sometimes regional) regulations. The International Standardisation Organisation (ISO) is co-ordinating working groups on soil quality (e.g. ISO TC/190) with the aim to identify a range of tests that would be acceptable for

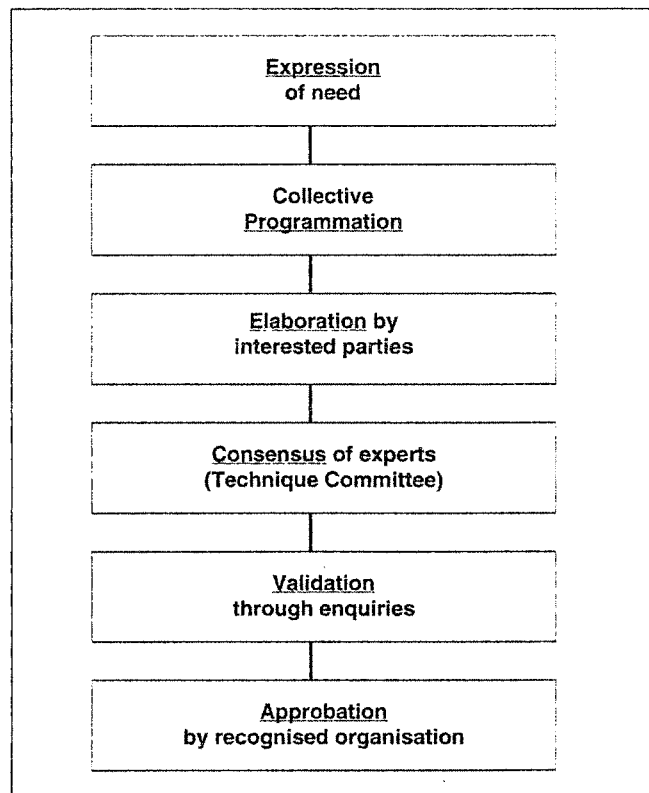


Fig. 1: Preparation process of a standard (adapted after Lombard 1999)

possible standardisation. Expert consultations and discussions are based on the selection of existing extraction schemes, e.g. EDTA, DTPA, neutral salt extractants, etc. which have to be first accepted as candidate standard tests (on the basis of their significance in risk assessment and risk management schemes used in field conditions), then demonstrated to be applicable to various matrices (easiness of use, ruggedness) and possibly tested by expert organisations. This approach requires extensive consultations and possibly interlaboratory testing of the selected candidate standard procedures.

Standardisation is achieved through the collaborative studies, which aim to demonstrate the applicability of candidate standards and to establish minimum technical requirements. Collaborative testing helps standardisation organisations to take the decision of adopting or not a given procedure as an international standard. As stressed below, RTD programmes (Research and Technological Development) may support pre-normative research that will have an impact on standardisation.

2 Collaborative Testing for the Harmonisation of Extraction Schemes

Basically, harmonisation work through collaborative testing forms the basis of further standardisation. The main difference is that harmonisation activities may be carried out with the aim to validate/optimize a common procedure (that will not necessarily become a formal standard), whereas standardisation is mandated by an official organisation. The

SM&T programme (Standards, Measurements and Testing) of the European Commission has given support to pre-normative research through feasibility studies (including interlaboratory testing) in a variety of sectors. This RTD programme was not responsible for the adoption of standards nor for their implementation, but acted as enabling organisation for improving the comparability of chemical measurements based on various analytical methods. These activities were indeed supporting standards that were mandated, e.g. by CEN, but many other projects, although they had a standardisation character, only aimed to reach a consensus among a given scientific community. The approach of the SM&T programme (also referred to as BCR throughout the text) was to improve the quality of analytical measurements in a stepwise manner, i.e. starting by small-scale projects and develop them into wide interlaboratory programmes (Quevauviller and Maier 1999). In the field of methods for soil and sediment fractionation studies, the principle followed has been to organise interlaboratory studies for testing the laboratory performance and then the applicability of selected extraction protocols. Stepwise interlaboratory programmes were thus launched for the determination of extractable trace metal contents and forms of phosphorus, involving around 30 laboratories from various European countries (Quevauviller 2001). The programme started by the distribution of simple solutions (for testing the performance of detection methods), followed by the distribution of soil and sediment reference materials for the determination of extractable trace element contents, following selected extraction protocols. The comparison was based on the strict use of the extraction protocols, with final determinations carried out by different techniques. The (soil and sediment) reference materials were tested to verify their homogeneity and stability for the tested parameters, which is one of the basic requirements for enabling a proper comparison to be performed. The collaboratively obtained values (using different techniques) were taken as the 'best representation of the state-of-the-art', i.e. they were taken as an excellent mean for laboratories to achieve comparability of their results to a recognised reference, which in this case is a consensus value represented by the mean of laboratory means and a given extraction protocol. This reference is by no means enabling traceability to the true value of the substance in the medium to be achieved, but it represents an indispensable ground for achieving comparability of measurements when using common extraction protocols.

More precisely, the BCR work on extraction methods for soil and sediment analysis first focused on the design of a (three-step) sequential extraction scheme for sediment analysis and the selection of single extraction tests for soil analysis for the determination of extractable trace metal contents (Ure et al. 1993). In a first stage, a literature search and a consultation with European experts were carried out on behalf of BCR (Ure et al. 1992). From the variety of schemes published, three single extraction procedures were selected for soil analysis, namely EDTA, acetic acid and ammonium acetate. In addition, three sequential extraction methods were selected and tested for sediment analysis, which resulted in the adoption of a simple three-step extraction protocol based on the scheme of Salomons and Förstner (Förstner 1993).

For both single and sequential extraction schemes, interlaboratory studies were designed and conducted with soil and sediment reference materials originating from the Joint Research Centre of Ispra, Italy (Ure et al. 1993). The interlaboratory programme was conducted between 1989 and 1994, and results are published in the literature (Ure et al. 1993, Quevauviller 2001). With respect to single extraction methods for soil analysis, EDTA and acetic acid extraction schemes led to comparable results, but the ammonium acetate extraction scheme did not result in a good between-laboratory agreement, probably due to the low contents of extracted metals and this scheme was not retained for further testing. A further interlaboratory study has been performed on a calcareous soil reference material, using EDTA and DTPA extraction procedures (Quevauviller et al. 1996). Both procedures resulted in a satisfactory agreement between the laboratories. Consequently, EDTA, DTPA and acetic acid extraction schemes were kept as candidates for harmonised protocols to be further tested and validated. The work on the sequential extraction scheme for sediment analysis was more complex since many errors resulted from a lack of compliance with the written protocol (e.g. differences in shaking time and speed). However, a reasonable, between-laboratory agreement was obtained after two trials (Quevauviller et al. 1994), which enabled one to consider that the three-step sequential extraction scheme was sufficiently robust and valid to yield comparable results. It was later recognised, however, that the scheme should be improved and possibly adapted for soil analysis; this represented a continuation of this programme which was concluded in 1999 and which resulted in an improved three-step sequential extraction scheme known as the 'BCR sequential extraction scheme'. The research work and the scheme are described in detail in the literature (Quevauviller 2001).

Another development related to extraction methodologies concerned the harmonisation of a common protocol for the determination of extractable forms of phosphorus in lake sediment (Ruban et al. 2001). The harmonisation work was based on the collaborative testing of four selected extraction schemes. The results of two interlaboratory trials (using various types of sediments) with expert laboratories pointed out that the best scheme would be an improved version of the Williams protocol which comprises five steps for the determination of, namely, NaOH-extractable P, HCl-extractable P, organic P, inorganic P and residual P. The commonly agreed upon protocol (named 'SMT protocol') is fully described elsewhere (Ruban et al. 1999, Quevauviller 2001) along with details on the interlaboratory trials. This is another illustration of successful harmonisation work, which establishes a common background of understanding for future-lake eutrophication studies.

3 Further Harmonisation Needs

As stressed above, the variety of existing extraction schemes for soil and sediment analyses often hampers the worldwide comparability of data. Efforts are being made to harmonise extraction methodologies used in environmental management, not only for soils and sediments, but also for waste analysis (Vandersloot et al. 1997). One aspect is collabora-

Table 1: Examples of extraction tests used for soil and sediment analyses

Matrix	Extraction procedure	Purpose of the test
Sludge, compost	Aqua-regia ('pseudo-total' element contents)	Risk assessment prior to spreading sludge onto agricultural soils
Soils	EDTA, DTPA, acetic acid	Trace metal mobility and soil-plant transfer studies
Soils	Weak extractants, e.g. calcium chloride, calcium nitrate, sodium nitrate, ammonium acetate	Plant uptake studies, soil deficiency assessment and remediation, fertility studies, risk assessment Risk assessment, evaluation of soil multifunctionality
Soils	Ammonium chloride, acid oxalate, ammonium acetate	Differentiation of lithogenic and anthropogenic origin of critical elements
Sediments	Aqua-regia ('pseudo-total' element contents)	Risk assessment, mapping (e.g. for marine monitoring)
Sediments	Sequential extraction schemes, e.g. BCR, three-step extraction protocol	Heavy metal mobility studies
Sediments	Sequential extraction schemes, e.g. SMT extraction protocol	Studies of phosphorus forms for lake eutrophication studies

tive testing (i.e. harmonisation with possible standardisation outcome), as described above, but the consensus for a range of extraction procedures to be possibly used as a common approach by laboratories working in different areas (e.g. soils, sludges, composts) is far from being achieved. An example of tests has been collected in various expert consultations (Quevauviller et al. 1996) and are listed in Table 1.

4 Validation Requirements for Extraction Methods

The concept of method validation in the case of operationally-defined procedures is primarily based on the acceptance, harmonisation and testing of selected extraction schemes, possibly proposed as standardised methods to official standardisation organisations. Validation can be carried out as described above, i.e. through the organisation of interlaboratory studies in which a group of laboratories receive 'real case' samples to be analysed following a strict protocol. The experience has shown that, while the tests carried out on some schemes resulted in a satisfactory agreement (e.g. EDTA, DTPA, acetic acid), this was not always achieved for other procedures, which demonstrated the inadequacy of the scheme(s) at the time that was tested, e.g. ammonium acetate but also weak extractants such as calcium chloride, sodium nitrate, owing to difficulties in applications and the high spread of results obtained by the laboratories (Ure et al. 1993). Another route for validating extraction methodologies is to make available reference materials that are certified on the basis of the schemes in question, i.e. for extractable forms of elements. The materials must be representative of real matrices (i.e. soils and sediments), and of verified homogeneity and stability (Quevauviller and Maier 1999). The BCR has developed activities in support of the validation of extraction methods since the beginning of the 90's (Ure et al. 1992), which led to the production and availability of four sewage-sludge amended soils (CRMs 483, 484, 600 and BCR-700) certified for their EDTA and acetic acid (or DTPA for CRM 600) extractable trace metal contents, two sediments (CRM 601 and BCR-701) certified for their extractable trace metal contents on the basis of the so-called BCR-sequential extraction scheme, and one sediment (BCR-684) certified for phosphorus forms on the basis of the so-called SMT protocol. The certification work carried out for these various materials (harmonisation of the extraction schemes, preparation of the materials, homogeneity and sta-

bility studies, certification analyses) is described in detail in a recent publication (Quevauviller 2001).

5 Additional Remarks

It is somewhat surprising to note the lack of co-ordination between 'harmonisation' (adoption of a common protocol based on scientific grounds, without official mandate) and 'standardisation' activities. The example of the BCR work on single and sequential extraction schemes for soil and sediment analysis illustrates this gap between scientific work aiming at harmonising methods and the work of standardisation technical committees (from ISO or CEN). Indeed, none of the schemes adopted by the soil and sediment scientific community were actually considered by ISO or CEN as possible candidates for international standards, whereas many of the members of these working groups actually participated in the BCR work! On the other side, extraction procedures that appear in regional or national regulations, e.g. calcium chloride, are being considered as possible ISO standards, whereas the interlaboratory agreement had been demonstrated to be very poor. This shows the problem that scientists have to face when they wear different 'hats', i.e. researcher from one side and data provider to regional or national administration from the other side. In other words, standardisation work in this field may concern methodologies that are proposed on the basis of regulatory requirements, but that do not necessarily correspond to the best of the state-of-the-art, whereas harmonisation work carried out on a voluntary basis may lead to an excellent interlaboratory comparability without, however, being considered as official standards. The funniest thing, perhaps, is to realise that commonly agreed protocols backed-up by CRMs for their validation, are actually widely used by the international scientific community as illustrated by the growing number of references on the 'BCR' or 'SMT' extraction schemes. The users might finally have the final word as was illustrated in the 80s with the adoption of the aqua-regia extraction method first as a DIN standard, then as an ISO standard: the aqua-regia method was used in a certification of trace elements with soil reference materials missing and the results were shown to be systematically biased (on the low side) in comparison to methods based on HF digestion. This highlighted the fact that the aqua-regia procedure did not achieve a full recovery of trace elements, but rather 'pseudo-

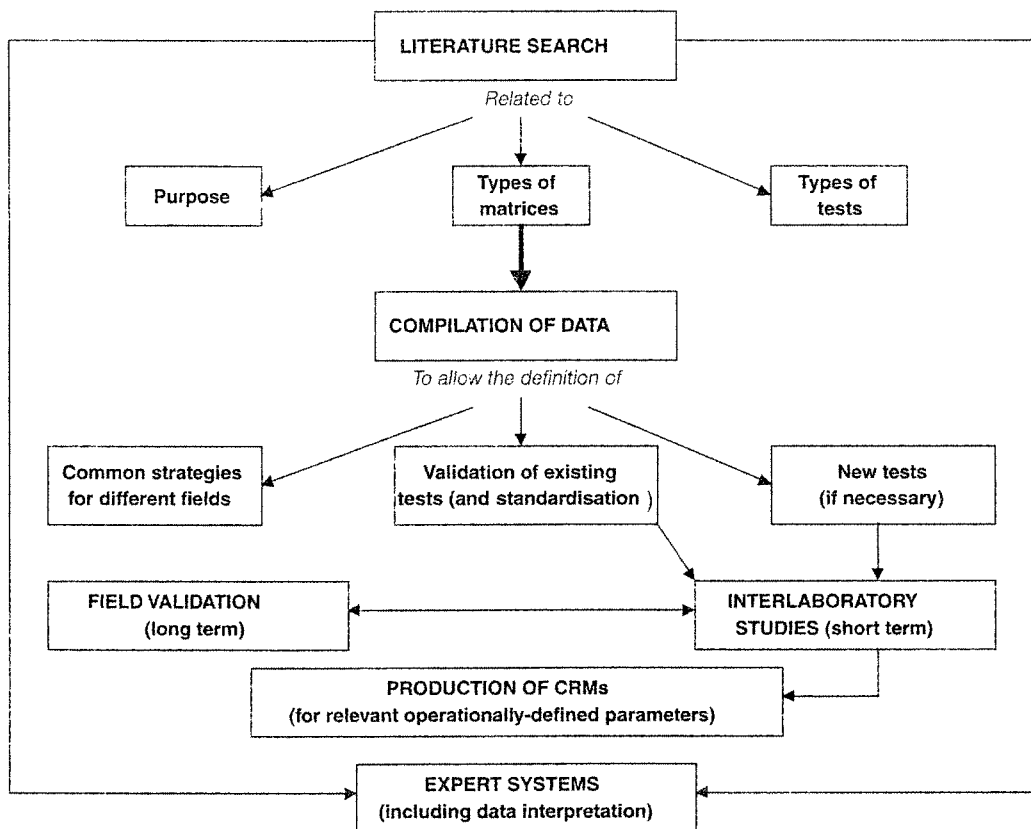


Fig. 2: Possible database searching system

total' contents. Consequently, a decision had been taken to certify not only the total trace element contents but also the 'aqua-regia soluble' contents in three different soils. After some years of extensive use of these materials, the aqua-regia procedure (as described in the BCR certification reports), became a 'standard', in practice and later an official standard.

6 Conclusions

There is an obvious need to pursue efforts for the validation of existing extraction schemes, e.g. by applying them to a wide variety of soil/sediment matrices. Further efforts are also needed to substantiate these schemes from practical field studies and questions related to their usefulness, etc. should be thoroughly investigated. Too many standard procedures are used as a result of regulations without being strongly supported by practical considerations such as usefulness in risk assessment and risk management in field application, easiness, user's friendliness (e.g. aqua regia is neither users friendly nor ecofriendly, complexing agents are not at all eco-friendly), scientific soundness, robustness, etc. One of the main trends is certainly the new approach followed by a group of EU experts who collaborate, in the frame of an EC-funded Thematic Network (Vandersloot et al. 1997). Methods should serve the purpose of estimation of risk of pollutants in given ecosystems. Such a network establishes clearly where collaborations are possible among disciplines for adopting common strategies for environmental risk assessment (van der Sloot et al. 1997). Standardisation might be the final goal for the establish-

ment of a range of tests 'fit-for-purpose' to various objectives, along the scheme shown in Fig. 2.

Another trend, which is a continuation of the efforts of harmonisation of leaching and extraction tests, is the required production of reference materials certified for operationally-defined parameters; this aspect is thoroughly described in the literature (Quevauviller and Maier 1999, Quevauviller 2001).

Acknowledgements. Some considerations expressed in this paper were based on results obtained in the frame of the EC funded projects MAT1-CT93-0007 and SMT4-CT96-2087 both co-ordinated by the University of Barcelona, of which the results are summarised in a recent publication (Quevauviller 2001).

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Received: July 19th, 2001

Accepted: September 7th, 2001

OnlineFirst: September 14th, 2001

Additional information

The table below presents a list of Certified Reference Materials that have been produced by the BCR (European Commission) for the quality control of extractable contents of 1. heavy metals (single extractions for soil analysis and sequential extraction scheme for sediment analysis) and 2. phosphorus in sediment. The CRMs are available from the Institute for Reference Materials and Measurements (<http://www.irmm.jrc.be>).

BCR material	Type of material	Extractant	Analytes
CRM 483	Sewage sludge amended soil	EDTA, acetic acid	Cd, Cr, Cu, Ni, Pb, Zn
CRM 484	Sewage sludge amended soil	EDTA, acetic acid	Cd, Cr, Cu, Ni, Pb, Zn
CRM 600	Calcareous soil	EDTA, DTPA	Cd, Cr, Ni, Pb, Zn
BCR-700	Organic rich soil	EDTA, acetic acid	Cd, Cr, Cu, Ni, Pb, Zn
CRM 601	Lake sediment	BCR-Sequential Extraction Scheme	Cd, Cr, Ni, Pb, Zn
BCR-701	Lake sediment	BCR-Sequential Extraction Scheme	Cd, Cr, Cu, Ni, Pb, Zn
BCR-684	Lake sediment	SMT Extraction Scheme (5 steps)	P