Chapter 4
Methods for the Determination of Heavy Metals and Metalloids in Soils

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Abstract This chapter explores the analytical methods currently available for the measurement of heavy metal content in soils, ranging from well-established techniques routinely applied in laboratories worldwide, to newly emerging approaches, and with emphasis on the need to select strategies that are 'fit-for-purpose' in terms of the information required. Included are guidelines for field sampling and for the storage of samples and avoidance of contamination. Brief information is provided on analytical techniques directly applicable to solid samples including neutron activation analysis, laser-induced breakdown spectrometry and X-ray-based methods. Suitable approaches to sample extraction for different situations are summarised (total digestion, pseudototal digestion, single and sequential extraction) together with examples of procedures involving hot-plate, block, bomb, and microwave apparatus. The use of extractants to assess (plant) bioavailability or (human) bioaccessibility of heavy metals in soils is discussed. Details are provided of the various types of atomic spectrometry that nowadays serve as 'workhorses' for trace metal determination in environmental chemistry, with particular emphasis on their principles, strengths, limitations and applicability. Included are flame and electrothermal atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry. The chapter also provides a brief introduction to the vast topic of speciation analysis, an area of particular interest for metals that can occur in different oxidation states e.g. Cr, or that have environmentally important organometallic forms e.g. Hg. Finally, some recommendations are given on strategies that researchers should adopt whenever possible to improve the quality of their analytical data.

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4.1 Introduction

The determination of heavy metals and metalloids in soil may be carried out for a variety of reasons. The total element content provides base-line knowledge of soil composition, with respect to which changes due to natural or anthropogenic processes can be assessed. Soils from metal-contaminated industrial sites may be analysed for legislative purposes, to assess risk to human health or the environment, or to monitor the success of remediation strategies. Agricultural chemists may wish to assess the availability of metals in soils, either as an indicator of potential plant deficiency or toxicity, or to determine the likelihood of metals' entry into the food chain of animals and man.

A potentially bewildering range of analytical techniques and methods now exist for the determination of heavy metals in soils. However, the most important factor to consider when deciding which approach to use is "What is the purpose of the study?" Knowing the type of information that needs to be obtained, or environmental question(s) to be answered, will guide the soil analyst towards analytical methods that are fit-for-purpose. For example, a portable, X-ray based spectrometer that measures total metal concentrations may be preferred for field analysis of metal-rich soil affected by mining waste, but a multi-step chemical extraction procedure, combined with advanced laboratory instrumentation, is likely to be more suitable for estimating the fraction of the metal content that will be bioaccessible in the human gastro-intestinal tract following accidental ingestion of a typical soil.

Many other factors may need to be considered when planning an analytical strategy including, but not necessarily limited to:

– sampling logistics (e.g. site access, sampling regime, safety)
– sample preservation, storage and preparation
– number(s) of analytes to be measured
– concentrations of analytes to be measured
– precision and accuracy required
– availability of laboratory apparatus and instrumentation
– cost of analysis
– time required to generate results.

This chapter describes current approaches to the determination of heavy metals in soils: it outlines their principles; discusses their strengths and limitations; provides information on their scope and applicability, and highlights some recent developments and applications.

Information on general [33, 75, 83, 98] and environmental [61, 96, 169] analytical chemistry can be found in several textbooks whilst detailed guidelines for handling analytical data are provided in [130]. It is particularly important to distinguish between accuracy and precision in analysis. Accuracy – the closeness of a measurement to the true value – indicates whether there is any systematic error ('bias') in a measurement.

It cannot be assessed for a sample where the analyte concentration is unknown. However, soil certified reference materials (CRM) of known composition are available commercially. Experienced laboratories will analyse these regularly to ensure that analytical methods remain under control (see Sect. 4.9).

Precision – the closeness of a set of measurements to one another – is a measure of the repeatability of an analysis. It indicates the magnitude of random error associated with the measurement, and is often expressed as the relative standard deviation (RSD) of n replicate measurements.

$$RSD = \frac{\sigma}{\bar{x}} \times 100$$

where σ is the standard deviation and $\bar{x}$ is the mean value.

The existence of random error means that the average of a set of analytical measurements is unlikely to be exactly equal to the true value. For this reason, experienced analysts rarely quote a mean value alone. Instead, it is usual to report a range within which the true value is likely to lie. This is termed the *analytical uncertainty* (some texts use the term *error*). It can be expressed as a confidence interval or by quoting the mean value ± the standard deviation.

Analytical techniques also suffer from background ‘noise’ from various sources. These can make a signal from the analyte difficult to distinguish from the blank. The limit of detection (LOD) below which concentrations cannot reliably be measured (and hence never should be reported) is often estimated by replicate analysis of a blank or low concentration standard and can be calculated from:

$$LOD = \frac{3\sigma_{BLANK}}{s}$$

where σ is the standard deviation of 10 replicate measurements
s is the slope of the calibration curve.

Analysts distinguish between the instrumental LOD, the lowest concentration that can be measured by a technique when the analyte in the required form (usually in solution) is presented to the instrument, and the procedural LOD, which takes account of any digestion and dilution steps required to prepare the test portion for analysis. The $\text{LOD}_{\text{PROCEDURE}}$ can easily be 100× or even 1,000× poorer (i.e. higher in concentration) than the $\text{LOD}_{\text{INSTRUMENT.}}$

4.2 Field Sampling

The first stage in the determination of heavy metals in soils is the collection of samples for analysis. The samples must be representative and collected using a suitable sampling regime i.e. one designed to match the purpose of the study. Even where this is the case, sampling can make a large contribution to the overall measurement uncertainty [69, 104, 163].

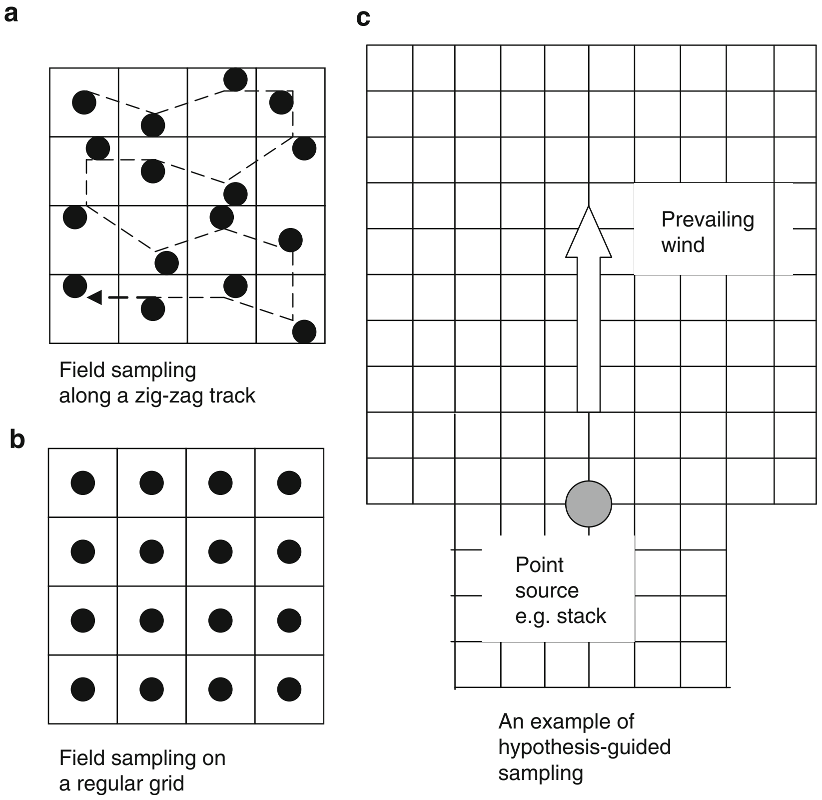


Fig. 4.1 Examples of sampling grids. (**a**) Field sampling along a zig-zag track. (**b**) Field sampling on a regular grid. (**c**) An example of hypothesis-guided sampling

If the goal is to obtain an average metal concentration, it is common to subdivide the field or plot (either notionally or physically with marker flags and twine) into segments (perhaps 20–25 segments for an area of 1–2 ha). A regular grid or herringbone pattern may be used. The vertices of the grid and locations of the sampling points may be obtained from a map or, nowadays, by use of a hand-held GPS, which has the advantage that the same sites may be easily revisited and sampled several times. Sample units are then collected, along a zig-zag path, either from a sampling point in each of the segments (Fig. 4.1a) or from a selection thereof (e.g. in the UK, arable soils are typically sampled by taking 25 cores per 5 ha, at 0–15 cm depth, in a W-pattern, avoiding any obvious ‘anomalous’ areas). These are combined to form a bulk sample, usually containing about 1 kg of field moist soil, although larger samples may be required for peaty or highly organic soils. Other studies aim to assess the spatial distribution of metals. In this case a grid may still be used, but one (or more) sample will usually be taken in each segment (Fig. 4.1b) and analysed individually, with associated increase in analytical workload and cost. Kriging [123] may be performed on the data to interpolate concentrations between sampling points.

In other situations, prior knowledge about the site under investigation, or the likely distribution of analytes therein, can be used to inform the sampling strategy. This is called *hypothesis-guided* soil sampling [186]. For example, if the aim of a study was to assess metal deposition onto soil from a point source such as a stack (or chimney), the sampling grid might be altered or extended to take account of prevailing wind direction, since contamination may reasonably be expected to be greater, and more extensive, in the downwind direction (Fig. 4.1c). A particularly challenge exists in designing sampling strategies appropriate for recently-derelict industrial sites. Detailed knowledge about the site history may be required e.g. previous locations of buildings, nature of processes carried out in various areas, types of compounds used etc.

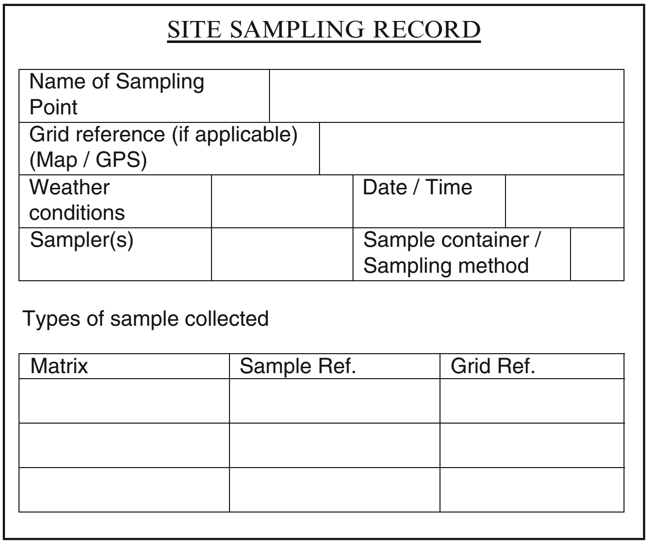
Sample units are taken to a uniform depth using an auger or corer (or, if these are unavailable, a spade or trowel). Arable land is usually sampled to the plough depth (typically 15 or 20 cm) whereas soil under grassland is sampled to a depth of only 7.5 or 10 cm [14]. A variety of sampling depths may be used at contaminated sites: sometimes surface soils are taken; sometimes trial pits are excavated to >1 m depth and material – which may be ‘made-up ground’ containing substantial quantities of materials such as brick, ash and clinker rather than true soil – removed from specific depths or visible layers for analysis.

Samples must be placed in proper containers. Polyethylene bags are suitable for the determination of most heavy metals, but should not be used if Hg is amongst the analytes because elemental mercury can pass through polyethylene and be lost or contaminate nearby samples. Glass bottles with screw-top lids are preferred in this case. Care must be taken to avoid all sources of contamination [173]. Carbon steel or aluminium sampling tools are generally preferred to stainless steel since the latter may incorporate large quantities of metals such as Cr, Mn, Mo and Ni; some plastics, notably PVC, should be avoided since they may contain trace metals; even paper towels may cause difficulties if they have been whitened with TiO_2 or dyed with a metal-containing compound. Tools should be rinsed with distilled water, or wiped clean, between samples.

Each sample must be labelled with a unique sample number, using a permanent marker, on the outside of the sampling bag (to avoid contamination of the soil with metal-containing inks). Other relevant details, such as sampling date and location (obtained from a map or GPS) should be recorded on site. Many organisations use a standard sampling pro-forma, an example of which is shown in Fig. 4.2. Sampling soils for trace analysis remains an active topic of research (see e.g. [217]).

4.3 Sample Preservation, Storage and Preparation

On arriving at the laboratory, soil samples are spread out (e.g. on polyethylene sheets in aluminium trays), aggregates are broken down, and the samples are dried. Air-drying, or drying at slightly elevated temperature (25°C) is usual. Higher temperatures may be used in the preparation of reference soils to improve their long-term stability. The dried soil is then passed through an aluminium or nylon



SITE SAMPLING RECORD

Name of Sampling Point			
Grid reference (if applicable) (Map / GPS)			
Weather conditions		Date / Time	
Sampler(s)		Sample container / Sampling method	

Types of sample collected

Matrix	Sample Ref.	Grid Ref.

Fig. 4.2 An example of a sampling pro-forma

sieve, usually of 2 mm mesh. Stones and other material >2 mm in diameter are discarded. The <2 mm (‘fine earth’) fraction is re-bagged and stored until required. Sub-samples may be ground or milled to smaller particle size (e.g. <150 μm) to ensure a more homogeneous test portion for direct methods of analysis, or expose a larger surface area for acid digestion. Representative sub-sampling of the dried soil can be carried out by coning and quartering or a mechanical riffler may be used. There is a minimum weight of soil, depending on the heterogeneity and grain size, that will be representative of the whole sample. Jackson [86] recommended that the test portion should contain at least 1,000 particles of the sieve opening size. Assuming a soil density of 1.3 g cm^{-3}, this corresponds to about 5 g for samples passed through a 2 mm sieve or about 0.7 g for samples passed through a 1 mm sieve. In practice, analysis of a larger test portion, say 20 g for soil sieved to 2 mm and 2–3 g for soil sieved to 1 mm, is desirable. Particular care is required when handling soils intended for speciation analysis to preserve the intrinsic form(s) of the analyte elements [50, 173, 209].

Contamination with analytes not originally present in the sample is a constant threat and can occur at any point in the analytical process [82]. The risk becomes more critical as the concentration to be measured decreases. The laboratory itself can be a source of heavy metals (used, for example, in some paints and plastics). Instrumentation for (ultra)trace element analysis such as inductively coupled plasma mass spectrometry (ICP-MS, see Sect. 4.7.5) should ideally be housed in a separate laboratory, remote from areas used to handle or digest soil samples. Avoiding the sample coming into contact with apparatus during processing is clearly impossible, but care should be taken to choose materials unlikely to cause problems in the particular analysis being undertaken e.g. avoid stainless steel when measuring Cr. Milling and grinding can be sources of various trace elements [58]. All glassware should be soaked, preferably overnight, in 5% HNO_3 and then rinsed with distilled water before use. High purity water (at least distilled or deionised) should be used at all times. Reagents should generally also be of high purity and should be run as blanks to check for contamination. Different chemical suppliers use different terms (e.g. Analytical Reagent, AnalaR etc.) for purified reagents and it is advisable to check the specification in the catalogue to choose the option with lowest concentrations of the analytes of interest.

4.4 Direct Methods of Analysis

Most methods for heavy metal determination in soils require the analytes to be presented to the instrument in solution. However there is growing interest in methods that can be applied directly to solid substrates, especially if these can be used in the field.

4.4.1 Instrumental Neutron Activation Analysis (INAA)

A sample is placed in a nuclear reactor by a remote-handling system and irradiated with a known flux of thermal neutrons. Stable isotopes can capture these neutrons and be transformed into radionuclides. The sample is then removed and the activation products are quantified, usually by γ-spectrometry. INAA was the first technique able to perform non-destructive, multi-element analysis on small (50–100 mg) solid samples with detection limits < 1 mg kg^{-1} (parts-per-million). Its applications include 'high-value' samples such as the soils recovered by Apollo astronauts from the lunar surface [91]. Disadvantages are the requirements for specialist irradiation facilities and highly-trained personnel, which limit the availability of the technique to national facilities or workers with access to a local research reactor. Recent applications include a study of the accumulation of Cr, Fe, Mn and Zn in arable soils amended with chemical fertiliser and animal manure [143], an investigation of soils affected by sulphides exploitation [113] and measurement of 16 trace elements to assess anthropogenic influence on agricultural soils in Argentina [142]. However, the scarcity of facilities, concerns over nuclear radiation, and improvements in other analytical techniques mean that the use of INAA is becoming less common.

4.4.2 X-ray Based Techniques

X-ray fluorescence spectrometry (XRF) is a powerful technique for multi-element analysis. It is relatively insensitive to sample form, essentially non-destructive, and able to detect elements with atomic numbers greater than about 8. In XRF, samples are irradiated with primary X-rays, usually from an X-ray tube or radioactive source. These eject inner electrons from atoms. The energy released when outer electrons ‘fall’ into these vacancies is observed as an X-ray fluorescence spectrum; the wavelengths observed are characteristic of the element(s) present. Two types of instrument are used: wavelength-dispersive X-ray fluorescence (WDXRF) [102, 192] and energy-dispersive X-ray fluorescence (EDXRF) [178, 214]. In WDXRF, the radiation emitted by the sample is diffracted in different directions and a (Si(Li)) detector is moved to detect X-rays with different wavelengths (alternatively, several detectors at fixed angles may be used). In EDXRF, a single detector is used in combination with a multi-channel analyser. EDXRF instruments have no moving parts and hence are cheaper than WDXRF, but WDXRF generally offers superior resolution. Samples for XRF analysis are ground finely and then either subjected to fusion, producing a glass for analysis [141], or compressed into pressed powder pellets [36, 192]. Matrix effects occur in XRF and mathematical corrections must be applied if accurate results are to be obtained [172].

A key advantage of XRF for measuring heavy metals in soils is the availability of instruments suitable for use in the field [92]. Portable XRF instruments have been used to measure As, Cu, Pb and Zn at a former waste site (now a sports ground used by children) [28] and in soils affected by mining [162]; As, Cu and Cr in soil polluted by chromated copper arsenate wood preservatives [118], and Cr, Cu, Mn, Ni, Pb, V and Zn in industrial soil [7]. Results obtained by portable XRF were found to be broadly similar to those of laboratory-based techniques, but the detection limits are poorer. The method is therefore most suited for rapid screening of contaminated sites to identify samples of interest that can then be taken back to the laboratory for more detailed or confirmatory analysis.

Recent developments in X-ray analysis [220] include total reflection-XRF in which the incident X-ray beam is directed at the sample surface at such an acute angle that it is reflected, thus reducing background interference problems caused by penetration into the bulk [224] and the advent of powerful, synchrotron-based techniques – reviewed recently by Lombi and Susini [112] – suitable for direct measurement, mapping and speciation of heavy metals in soils. Indeed, one of the first environmental science experiments performed using the new ‘Diamond’ light source in the UK was a study of the speciation of Pb and Zn in soil undergoing remediation with bone meal [136].

4.4.3 Laser-Induced Breakdown Spectroscopy (LIBS)

This is an emerging form of atomic emission spectrometry (see Sect. 4.7.1) applicable to a wide variety of sample types, including solids such as dusts and soils, with minimal sample preparation [108]. A high powered, pulsed laser (typically a Nd:YAG at either 1,064 nm or frequency-doubled to 532 nm) is used to ablate the surface of the sample. This forms a high temperature microplasma in which the

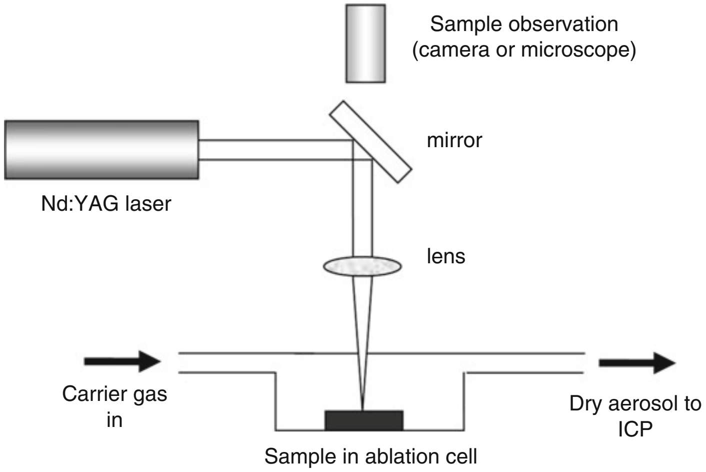


Fig. 4.3 Laser ablation inductively coupled plasma mass spectrometry

constituents of the ablation plume are atomised, ionised, excited, and then emit light of characteristic wavelengths. This light is measured after a short delay (around 500 ns) during which the intense broadband emission from the plasma decays. Comparisons between soil heavy metal concentrations obtained by LIBS and by other methods suggest that the technique shows promise [27, 188] but further optimisation and a better understanding of the behaviour of analytes in the plasma [60], together with improvements in accuracy and LOD [54, 80] are required. A particular advantage of LIBS, in common with XRF, is the potential to develop field-portable instruments [34, 73].

4.4.4 *Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)*

Conventional (solution sample) ICP-MS is described in Sect. 4.7.5. However there is also considerable current interest in the use of lasers to generate ions for introduction to the plasma. This allows the technique to be applied to a wide variety of solid samples, including soils, plants and related materials, yielding important information on, for example, the distribution of heavy metals in response to pedogenic processes [183]. As in XRF, the sample must be finely ground before analysis. The particle size has a strong influence on the quality of the measurement [88] and use of <1 μm diameter particles is recommended [9]. The powdered sample is pressed into a pellet, sometimes with the addition of a binder, and placed in an ablation chamber (Fig. 4.3). Early workers [11, 16] used aqueous calibrants for LA-ICP-MS. However, nowadays, it is common to prepare matrix-matched standards by spiking soils with appropriate analytes and internal standards [88, 107].

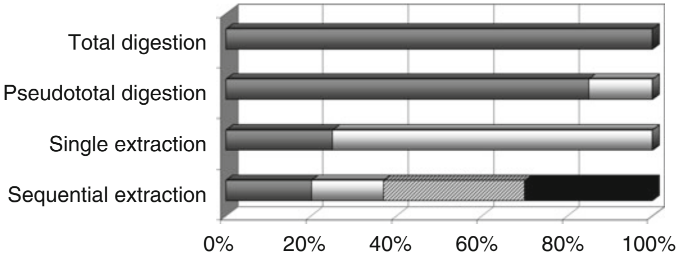


Fig. 4.4 Some approaches to the determination of heavy metals in soils (After [210])

4.4.5 Slurry Sampling

This is an approach that allows solid samples to be analysed by techniques such as atomic spectrometry that usually require solution samples. In essence, the sample is ground finely, suspended in a suitable medium, and the resulting slurry is introduced into the instrument in a similar fashion to solution samples. The method is particularly useful for refractory samples that are difficult to digest, but great care must be taken to optimise the sample particle size distribution, stablise the slurry, and properly calibrate the instrument response [52]. Recent reviews are available discussing the use of slurry sampling with electrothermal atomic absorption spectrometry (ETAAS) [26], with ICP-based techniques [52, 180], and with hydride generation [125].

4.5 Sample Digestion and Analyte Extraction

Digestion or leaching to transfer the analytes into solution is a necessity for most instrumental methods of analysis. The nature of the extractant used to release the metals from the soil matrix is of vital importance: different reagents liberate metals from different soil components and hence provide different types of information. Some approaches to the measurement of heavy metals in soils are summarised in Fig. 4.4 and discussed in the following sections.

4.5.1 Total Digestion

Total element contents are of interest, for example, in geochemical surveying [135] and to assess geogenic metal concentrations [97]. Hydrofluoric acid is used for total digestion of soil samples because it can dissolve silicates. The entire sample is solubilised and the total metal content released for measurement. Special precautions are required when handling HF: it cannot be stored or used in glass vessels; fume hoods may have to be specially adapted to avoid corrosive vapours attacking the components of the ventilation system, and use of appropriate personal protective equipment (including the provision of calcium gluconate HF antidote gel) is vital due to the serious nature of HF burns. An oxidising acid such as nitric or perchloric is often used in combination with HF to aid dissolution of organic matter and sulphides.

Another approach for total dissolution of soil samples is fusion. Typically, a small sample (e.g. 0.1–0.2 g) of ground (<100 μm particle diameter) soil is placed in a platinum crucible with ~0.8 g of lithium metaborate and heated to around 1,000°C. The sample dissolves in the molten flux. This may be quenched (with care!) by pouring it into a solution of nitric acid, or the flux may be allowed to cool and the resultant glass later dissolved in nitric acid. The acid solution is then made up to a set volume for analysis. The method tends to be reserved for samples containing refractory minerals e.g. chromite [135] that are difficult to bring into solution by other means.

4.5.2 Pseudototal Digestion

In pollution studies the goal is often to assess anthropogenic input, or estimate the maximum amounts of metals that could hypothetically be mobilized and transported in the environment and affect a receptor. Pseudototal (PT) digestion with mixtures of hydrochloric acid, nitric acid or hydrogen peroxide is widely used for this purpose. Although primary silicates are not dissolved, metals associated with most other major soil components are liberated.

In a typical PT digestion, a few grams of soil are weighed into a vessel. The soil is moistened with water and then *aqua regia* (a mixture of 3 parts HCl to 1 part HNO_3) added. The vessel is allowed to stand overnight, then the temperature is raised and the contents maintained under reflux for 2 h. After being allowed to cool, the digest is filtered into a volumetric flask, the residue washed with dilute nitric acid and the washings combined with the filtrate. Finally, the digest is made up to the mark with distilled water or dilute HNO_3 ready for analysis.

Both total and PT digestions may simply be carried out using beakers topped with watch glasses (made of PTFE in the case of HF) on a hot-plate placed in a fume cupboard. The digestion needs to be monitored and extra acid added to compensate for losses due to evaporation. Further additions of, for example, HNO_3 might also be necessary if the soil had a high organic content. However, many soil laboratories use more sophisticated apparatus, such as block or bomb digestors, and laboratory microwave ovens

Aluminium and graphite block digestors are able to extract metals from soils at controlled temperature. The digestion may be performed in disposable calibrated vessels that can be placed directly onto the autosampler of, for example, an ICP instrument, or the sample may be filtered prior to analysis. These digestors offer savings in time and increased sample throughput for laboratories handling large numbers of soil samples, although the fact that each digestion tube can hold only a few grams of soil may be a limitation for some applications. Tubes are usually topped with disposable watch glasses. However, specialised, non-disposable tops can be used to minimise loss of volatile species, for example in the measurement of Hg.

Bomb digestion, in which a soil sample and appropriate acid mixture are placed in a sealed vessel made from PTFE, stainless steel or aluminium and heated on a hotplate or in an oven, is also still popular. Because the vessel is sealed, loss of volatile species is minimised and there is less opportunity for the sample to become contaminated. An obvious danger is that, if the vessel exceeds its maximum operating pressure, it may explode. Bomb digestors should therefore always be operated exactly according to the manufacturer's recommendations.

The use of microwave-assisted sample digestion is now widespread. Microwave energy is absorbed directly by the solution, rather than there being a delay whilst heat is transmitted from an external source. Hence, it offers the advantages of speed, uniform heating of the sample, and contamination avoidance (provided closed vessels are used). Initially, many soil laboratories used domestic i.e. kitchen microwave ovens and home-made PTFE digestion vessels. Nowadays, commercial laboratory microwave apparatus is available. In a typically microwave-assisted PT digestion, 1 g of soil would be placed in a PTFE digestion vessel, 20 mL *of aqua regia* added and, after any initial vigorous reaction has subsided, the vessel would be placed in the microwave cavity and heated for, perhaps, 20 min. The vessel would then be removed, allowed to cool, and the contents filtered into a volumetric flask. Modern commercial microwave digestion systems can digest up to 40 samples simultaneously. The power is controlled by a temperature sensor that monitors all of the vessels in the cavity. The heating program and acid mixture can be optimised, for example by analysis of suitable CRM [15, 77, 179].

Several authors have compared digestion methods to determine those most suited to particular applications e.g. [103, 222]. For calcareous soils, Mico et al. [129] obtained higher extraction efficiencies, but poorer precision, using an open-vessel block digestor than closed-vessels in a microwave system, whilst Marin et al. [122] discovered significant underestimation of Al in the presence of HF when comparing microwave digestions with various acid mixtures. For Florida soils, Chen and Ma [32] obtained recoveries in the order: microwave (*aqua regia* + HF) > microwave (*aqua regia*) > hotplate (*aqua regia*). Useful general guidelines on preferred digestion approaches for soils of different composition (organic matter, carbonate content and closeness of metal concentrations to legislative limits) are provided by Sastre et al. [182].

4.5.3 Single and Sequential Extraction

There is considerable interest in assessing the fractions of the total metal content associated with specific soil mineral phases. This information is now beginning to be available through application of direct methods of speciation analysis (see Sect. 4.8). However, for many years, soil scientists have tried to infer it by application of selective chemical extractants. Although this approach has produced much useful information, it is important to be aware that the reagents used are rarely completely specific. It is therefore often beneficial to consider extractants as targeting not precise mineral phases, but specific ‘pools’ or ‘reservoirs’ of heavy metals in the soil, each of which will have different solubility, mobility and potential environmental impact. A selection of approaches and reagents that have been used to isolate heavy metals associated with different soil phases are discussed below. Further details and numerous additional examples are available in Ure and Davidson [210] and in the recent, comprehensive, review by Rao et al. [165].

The soil solution contains the most mobile and readily plant-available species, including free ions and metals complexed with soluble organic matter and other ligands. It can be isolated by filtration [156], dialysis [90, 115], centrifugation [197] or displacement [114]. Metal concentrations are generally low and sensitive analytical techniques such as ICP-MS may be required for quantification. Water-soluble species may be isolated by water extraction [196] (hot water for boron [41]) or treatment with a dilute salt solution e.g. 0.01 mol L^{-1} $CaCl_2$ [115].

Exchangeable metals – those held by electrostatic interactions on both inorganic and organic soil components – can be liberated by treatment with cations. A variety of extractants have been recommended, including 0.1 mol L^{-1} $Ca(NO_3)_2$ [17], 0.1 mol L^{-1} $CaCl_2$ [187], 1.0 mol L^{-1} NH_4NO_3 [68] and 1.0 mol L^{-1} $Mg(NO_3)_2$ [149]. Use of an acetate salt e.g. 1.0 mol L^{-1} ammonium acetate at pH 7 [12] is advantageous since acetate can complex the liberated analytes and prevent re-adsorption [46] but may not be applicable in all soils [164].

Organic matter can be destroyed by treatment with hydrogen peroxide/nitric acid [149] or sodium pyrophosphate [159], thus liberating any associated heavy metals into solution for quantification. Alternatively, metals can be extracted by a chelating agent such as ethylenediaminetetraacetic acid (EDTA) [159] or diethylenetriaminepentaacetic acid (DTPA) [164] although neither reagent is entirely phase-specific. Carbonates are susceptible to dissolution in acid e.g. 1.0 mol L^{-1} acetic acid [12]. Hydroxylammonium chloride can release metals sorbed on manganese and iron (hydr)oxides, with different concentrations used to target separately the amorphous and crystalline forms [47]. Tamm’s reagent (acidified ammonium oxalate) has, for almost a century, been applied to dissolve iron (hydr)oxides [215], although some heavy metals, notably lead and cadmium, form insoluble oxalate species and so may precipitate from solution after extraction [38].

One way to improve the selectivity of soil extraction is to apply not one, but a series of reagents, in order of increasing ‘vigour’. Metals released early in the series are those more weakly bound to the soil and so have greatest potential mobility. Sequential chemical extraction can sub-divide the soil metal content into pools, nominally associated with different mineral phases and which are likely to respond in different ways to changes in environmental conditions such as pH or redox potential. A wide variety of sequential extraction procedures have been proposed since the early work of Tessier et al. [202]. These are summarised in detail in recent

Table 4.1 The revised BCR sequential extraction scheme[a]

	Reagent	Fraction	Nominal target phase(s)
Step 1	0.11 mol L^{-1} acetic acid	Exchangeable, water and acid soluble	Soluble and exchangeable cations, and carbonates
Step 2	0.5 mol L^{-1} hydroxylammonium chloride at pH 1.5	Reducible	Iron and manganese oxides
Step 3	H_2O_2 (85°C) then 1.0 mol L^{-1} ammonium acetate	Oxidisable	Organic matter and sulphides
(Step 4)[b]	*Aqua regia*	Residual	

[a] For the full protocol, see [167]

[b] Although not officially a step in the extraction, it is recommended that the residue from step 3 be digested with *aqua regia* and the sum of the fractions compared with results obtained from *aqua regia* digestion of a separate test portion of the sample

reviews [63, 165, 177]. Difficulties in comparing results obtained by different protocols led to the development, under the auspices of the Commission of the European Communities Community Bureau of Reference (BCR), of a harmonised three stage extraction [212] which was later modified to improve the dissolution of iron oxides in step 3 [176]. The revised BCR sequential extraction [167] is outlined in Table 4.1. A reference material, lake sediment BCR 701, certified for metals extractable by the procedure, is available.

Sequential extraction has provided considerable insight into the behaviour of heavy metals in soils. For example, the BCR scheme has recently been applied to assess potential mobility of Cd, Cr, Cu, Ni, Pb and Zn in agricultural soils from Greece [67]; to investigate the influence of parent material and pedogenic processes on distribution of heavy metals in soils from Iran [139]; to study temporal changes in soils contaminated with pyritic sludge and acidic wastewater released by an opencast mine in Spain [158], and to explore interactions between soil, meltwater and lakes in Antarctica [119]. The procedure has improved understanding of urban geochemistry [39, 94] and, when combined with isotopic analysis, shed light on the transport and mobility of depleted uranium (DU) at weapons testing sites [145]. In the field of soil remediation, the influence of EDTA on uptake of Ca, Cu, Fe, Mn, Pb and Zn by *Taraxacum officinale* (dandelion) [137] and the potential of the iron reducing microorganism *Desulfuromonas palmitatis* as a biostabilisation agent for chromate contamination [148] have been investigated.

The user of sequential extraction must always be aware of the inherent limitations of the approach, including potential redistribution of analytes, non-selectivity of reagents, incomplete extraction and formation of artefacts. A critical review of the field has recently been published [10] that includes the following general recommendations for use of sequential extraction procedures:

(i) use standard protocols e.g. the BCR extraction, precisely as recommended
(ii) use available quality control measures e.g. mass balance calculations and CRM
(iii) report results in terms of operationally-defined fractions e.g. ‘reducible phase’ and not specific minerals e.g. ‘iron oxide bound’

(iv) present data as absolute concentrations because fractionation patterns can be misleading
(v) use the approach in comparative studies e.g. soil before and after amendment
(vi) be cautious in drawing inferences about bioavailability in the absence of corroboratory evidence e.g. results of pot cultivation experiments etc.

4.5.4 Bioavailability and Bioaccessibility

There is increasing interest in the determination of the bioavailable metal content in soils because, when assessing risk, it is the fraction able to enter and affect the biological systems of an organism that is of concern, not the total metal content [150, 184]. Unfortunately, the term *bioavailable* has different meanings in different disciplines and, perhaps as a result, it is sometimes used rather non-specifically in soil literature. It is vital that workers investigating bioavailability should always make clear the target organism(s), chemical species and exposure route(s) being considered.

In agriculture, a high proportion of soil analyses are conducted for the purpose of estimating the levels of essential trace elements that are currently plant-available. This allows appropriate nutrient management decisions to be made concerning, for example, whether a particular crop can be grown or whether trace element deficiencies are likely to occur, in which case soil amendment with chemical fertilisers may be required. A variety of empirically-derived extraction procedures have been developed to estimate plant availability of heavy metals (Table 4.2) using similar reagents to those discussed in Sect. 4.5.3. These can also be used to assess the suitability, or monitor the progress, of phytoremediation strategies applied to contaminated land.

Numerous studies have demonstrated that the optimal extraction procedures (i.e. those providing data most closely correlated to that obtained in pot cultivation experiments) are specific to particular elements, crops, and even soils types [6, 13, 89, 133, 219]. Takeda et al. [198] compared metal uptake in plants with results of soil extraction using acids (1.0, 0.1 and 0.01 mol L^{-1} HNO_3), a chelating agent (0.05 mol L^{-1} EDTA), neutral salt solutions (1.0 mol L^{-1} NH_4OAc, 1.0 mol L^{-1} NH_4NO_3, 0.01 mol L^{-1} $CaCl_2$) and water. They found strong correlations only for a few elements, and only for some of the neutral salt extractions. Both McBride et al. [127] and Menzies et al. [128] also recommended neutral salt solutions as the best 'general purpose' soil extractant for the estimation of phytoavailability. Other workers proposed the Mehlich 3 reagent (a mixture of 0.2 mol L^{-1} acetic acid, 0.25 mol L^{-1} NH_4NO_3, 0.013 mol L^{-1} HNO_3, 0.015 mol L^{-1} NH_4F and 0.001 mol L^{-1} EDTA) [132], or a rhizosphere-based method involving extraction with a mixture of low molecular weight organic acids (acetic, lactic, citric, malic and formic acids in the molar ratio 4:2:1:1:1 at a combined concentration of 0.01 mol L^{-1}) [59]. There is also recent interest in the use of passive sampling devices based on diffusive gradients in thin films to predict plant uptake [29, 153].

Table 4.2 Examples of extractants used to estimate plant-available heavy metals

Extractant	Elements	Plant	Reference
Water	B	*Brassica chinensis, Agropyron elongatum*	[225]
Water	Cd, Cu, Mn, Zn	Native plants	[218]
Water	As, Cd, Cr, Cu, Ni, Pb, Zn	Maize	[87]
0.005 M DTPA[a]	Cd, Cu, Mn, Ni, Pb, Zn	*Brassica chinensis, Agropyron elongatum*	[225]
0.005 M DTPA	Cd, Cu, Fe, Pb, Zn	Tomato	[99]
0.005 M DTPA	Cu, Zn	Rice	[228]
0.005 M DTPA	Hg	Rice – cabbage – radish	[89]
0.005 M DTPA	Cd, Cu, Mn, Zn	Native plants	[218]
0.005 M DTPA	Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Wheat	[18]
0.01 M acetic acid	Cu, Ni	Wheat	[219]
0.01 M citric acid	Cu, Ni	Wheat	[219]
0.01 M oxalic acid	Cu, Ni	Wheat	[219]
0.01 M tartaric acid	Cu, Ni	Wheat	[219]
0.01 M organic acid mixture	Cu, Pb, Zn	Barley	[117]
0.01 M $CaCl_2$	As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn	Potential bioavailability	[207]
0.01 M $CaCl_2$	Cd	Oats	[71]
0.01 M $CaCl_2$	Cu, Pb, Zn	Barley	[117]
0.01 M $CaCl_2$	Cu, Pb, Zn	Ryegrass	[4]
0.01 M $CaCl_2$	As, Cd, Cr, Cu, Ni, Pb, Zn	Maize	[87]
0.05 M EDTA	Cu, Ni	Wheat	[219]
0.05 M EDTA	Cu, Pb, Zn	Barley	[117]
0.05 M EDTA	As, Ni, Pb	*Rubus ulmifolius*	[124]
0.1 M $CaCl_2$	Hg	Rice – cabbage – radish	[89]
0.1 M HCl	Hg	Rice – cabbage – radish	[89]
0.4 M LiCl	Cd, Cr, Cu, Ni, Pb	Various food crops	[53]
0.5 M $Ca(NO_3)_2$	Cd, Cu, Fe, Pb, Zn	Tomato	[99]
0.5 M NH_4Ac, 0.5 M acetic acid 0.02 M EDTA	Cu, Pb, Zn	Ryegrass	[4]
1.0 M $MgCl_2$	Cu, Ni	Wheat	[219]
1.0 M NH_4OAc	Cu, Ni	Wheat	[219]
1.0 M NH_4OAc	Hg	Rice – cabbage – radish	[89]
1.0 M NH_4HCO_3	Cd, Cu, Mn, Ni, Pb, Zn	*Brassica chinensis, Agropyron elongatum*	[225]
1.0 M NH_4NO_3	Cu, Ni	Wheat	[219]
1.0 M NH_4NO_3	Cd, Cu, Pb, Zn	Potential bioavailability	[100]

[a] Actually a 0.005 M DTPA, 0.01 M $CaCl_2$ and 0.1 M triethanolamine buffered (pH 7.3) solution [111]

Table 4.3 Examples of physiologically-based extractions used to assess the human bioaccessibility of heavy metals in soils

Procedure	Mouth	Stomach	Intestine
1 [116, 134]	n/a	0.4 M glycine at pH 1.5; 1 h	n/a
2 [19, 147, 174, 221]	n/a	Pepsin, citrate, malate, lactic acid, acetic acid; pH 1.5; 1 h	Stomach + pancreatin, bile salts; pH 7; 2–4 h
3 [25]	KCl, NaH_2PO_4, KSCN, Na_2SO_4, NaCl, NaOH, urea, amylase, mucin, uric acid; pH 6.5; 15 min	NaCl, NaH_2PO_4, KCl, $CaCl_2$, NH_4Cl, HCl, glucose, gluouronic acid, urea, glucosaminehydrochloride, bovine serum albumin, mucin, pepsin; pH 0.9–1.0; 1 h	NaCl, $NaHCO_3$, KH_2PO_4, KCl, $MgCl_2$, HCl, urea, $CaCl_2$, bovine serum albumin, pancreatin, lipase; pH 7.4; 4 h

Of increasing recent interest is the estimation of human oral uptake of heavy metals following ingestion of soil. Ingestion may occur either accidentally, due to poor hygiene and consumption of inadequately washed foodstuffs, or deliberately due to geophagia (soil consumption for medicinal or religious purposes) and pica (an eating disorder in which the sufferer consumes non-food substances). It is important to distinguish between *bioavailability* (the fraction of the oral dose that is absorbed into the systemic circulation [171]) which can only be measured by blood metal analysis, and *bioaccessibility* (the fraction that is soluble in the gastrointestinal environment and thus available for absorption) which can be estimated *in vitro*.

A variety of extraction procedures have been developed to simulate conditions in the human gastro-intestinal tract and thus assess human oral bioaccessibility of heavy metals in soils [85, 146, 226]. These are performed at 37°C with stirring or shaking, but differ in complexity, reagents used, duration and number of compartments simulated. Procedure 1 in Table 4.3, sometimes called the simplified bioaccessibility extraction test (SBET) method has recently been applied to urban soils in Sevilla and Torino [116] and to soils from a transect across the United States and Canada [134]. Procedure 2, derived from the physiologically-based extraction test (PBET) of Ruby et al. [174] has been used to assess human bioaccesibility of As in soil with high geogenic concentrations [147] and of As [221] and Pb [19] at sites affected by mining and ore processing. Procedure 3 is the emerging unified BARGE (Bioaccessibility Research Group of Europe) method, results of which have recently been compared with both total As concentrations and As concentrations in earthworms at sites in the UK [25].

Unfortunately, rather few of the physiologically-based extractions have so far been validated by comparison with *in vivo* studies and then only for a limited range of analytes e.g. the PBET of Ruby et al. has shown correlations with animal models for As and Pb [174]. Also, similar to sequential chemical extraction in the 1990s, the approach suffers from limitations, including needs for harmonisation of analytical methods, development of standard protocols and CRMs. These topics are currently being addressed, for example by the EU BARGE consortium [227].

4.6 Analyte Preconcentration and Separation

Matrix components may interfere with the determination of heavy metals in soils, in which case it may be necessary to separate the analyte(s) from potential interferents prior to measurement. There are also situations where analytes are present at concentrations too close to (or below) the LOD of available instrumental techniques. Preconcentration methods can increase the concentration of analyte in the solution presented to the instrument, allowing accurate quantification. It is of course necessary to know the preconcentration factor achieved, so that the original analyte concentrations can be calculated.

Procedures for the preconcentration of heavy metals in soil extracts and digests tend to be based on solid phase extraction, co-precipitation, or cloud-point extraction (for recent examples see [23]). In solid phase extraction, a selective sorbent is prepared by functionalising a supporting medium with chemical moieties able to complex selectively the metal(s) of interest. The sorbent is packed into a column and the soil extract passed through. Analytes are retained but interferents are not. The analytes can then be eluted for analysis. If the volume of eluant used is smaller than the volume of extract originally loaded, then preconcentration will be achieved. An alternative approach is to add the complexing agent to the soil extract, rather than functionalise the sorbent. Co-precipitation procedures involve the trapping of analytes (or interferents) on a solid carrier. In cloud point extraction a surfactant is added to the soil extract, together with a selective chelating agent. Under appropriate conditions, the mixture partitions into a surfactant-rich phase, in which the metal complexes are concentrated, and a dilute aqueous phase [42].

4.7 Instrumental Techniques for Measurement of Heavy Metals

Most techniques for measuring heavy metals in soils require the sample to be dissolved or leached to produce a solution for analysis and the instrument to be calibrated with a series of standard solutions of known concentration. These often can be prepared in dilute acid solution e.g. 5% HNO_3. However, in some analyses, the presence of extractant reagents alters the response of the instrument (Fig. 4.5a). In this case, calibrants must be reagent-matched. In other situations, components of the soil matrix, co-extracted with the analytes, may interfere in the analysis. Reagent-matching will not overcome this type of interference; instead it is necessary to matrix-match the standard solutions (i.e. they should contain all the same components as the soil extract, but no analyte). Since this is rarely possible, analysis is instead performed by the method of standard addition (Fig. 4.5b). Known concentrations of analyte are added to aliquots of the soil extract. The graph obtained is extrapolated and the (positive value of the) point where it crosses the x-axis is the analyte concentration in the extract.

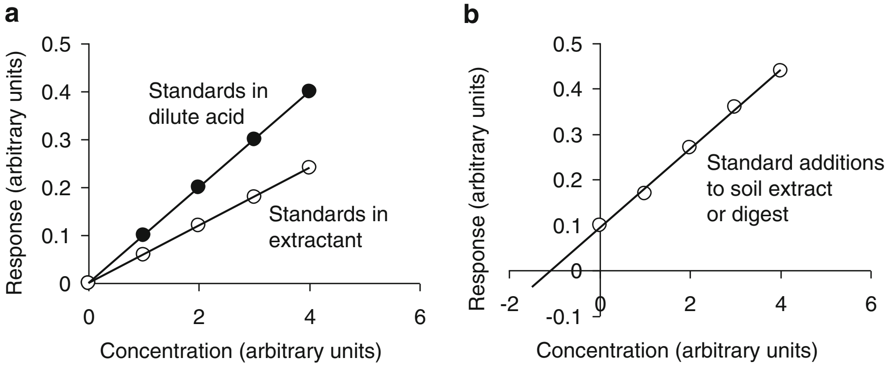


Fig. 4.5 Calibration in atomic spectrometry (**a**) a suppressive interference caused by the extractant matrix (**b**) calibration by standard addition

4.7.1 Atomic Spectrometry

Atomic spectrometry involves measurement of the electromagnetic radiation absorbed or emitted by free atoms when their valence electrons undergo transitions between atomic energy levels [45, 106]. In atomic absorption, energy is transferred from a photon to an atom, causing an electron to be promoted to an excited state. In atomic emission, electrons in an excited state de-excite and their excess energy is emitted as photons. The number of atoms with electrons in higher energy levels increases with temperature, and so spectroscopic techniques involving atomic absorption tend to be conducted in the (relatively) low temperature environment of a combustion flame, whereas emission techniques require higher temperatures such as those available in plasmas. Because different types of atom have different electronic configurations, each element absorbs and emits light at characteristic wavelengths. The amount of light absorbed or emitted is proportional to the concentration of analyte present.

4.7.2 Flame Atomic Absorption Spectrometry (FAAS)

A typical atomic absorption spectrometer consists of a light source to supply photons, an atom cell to create free analyte atoms, a monochromator to isolate the wavelength of interest, and a photo-multiplier tube detector (Fig. 4.6). The light source is usually a hollow cathode lamp (HCL) (Fig. 4.7) although electrodeless discharge lamps (EDL) are also used. In an HCL, the cathode is made from, or coated with, the analyte element. A voltage is applied between anode and cathode, producing an electrical discharge in the fill gas (typically neon or argon at 1–5 torr). Noble gas ions are accelerated towards the cathode where they cause sputtering. When excited atoms removed from the surface de-excite, a line emission spectrum

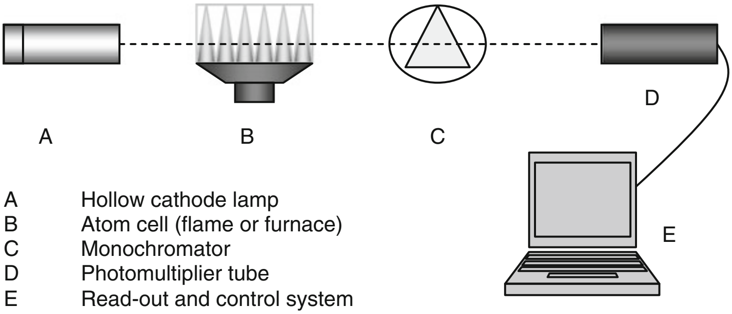
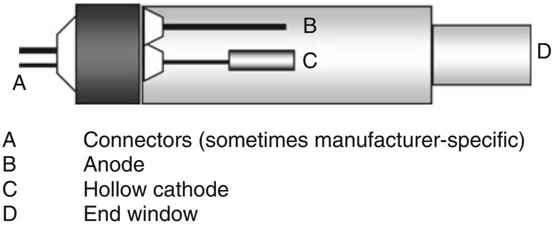


Fig. 4.6 Schematic diagram of an atomic absorption spectrometer

Fig. 4.7 Schematic diagram of a hollow cathode lamp



characteristic of the cathode element is produced. This light is directed through the atom cell, where it can be absorbed by analyte atoms. Spectral lines are broadened relative to natural widths by the Doppler effect (related to temperature) and collisional effects (related to temperature and pressure). Since the hollow cathode lamp operates at lower pressure and temperature than typical atomisers, the emission linewidth from the lamp is narrower than the analyte absorption profile in the atom cell. Hence, all of the light can be absorbed.

FAAS is widely used for determining heavy metals in soils. The atom cell is a combustion flame. The most common type is the air-acetylene flame (T ~2,200°C). Air and fuel are pre-mixed in a spray chamber and then flow past a nebuliser (a narrow metal tube connected to a plastic tube, which draws the sample up at a rate of about 5 mL min^{-1}). A proportion ($<10\%$) of the aerosol generated – that part containing the smallest, most uniformly-sized droplets – is swept into the base of the burner and aspirated into the flame. At least a few milliliter of sample solution are required to perform a measurement, although this can be reduced by the use of pulse nebulisation.

An alternative flame uses nitrous oxide-acetylene (T ~ 2,900°C). This provides better atomisation efficiencies but is less safe because of the higher burning velocity – hence a shorter burner head is used (5 cm *cf.* 10 cm for air-acetylene) – and also gives out a more intense background emission spectrum. Its use tends to be reserved for elements that are difficult to atomise with air-acetylene due to formation of thermally stable oxides, such as Al and Mo. Whichever flame is used, the conditions (fuel flow and burner height) have to be optimised for each analyte (and for different reagent matrices) to maximise the atomisation efficiency.

FAAS is subject to spectral, physical and chemical interference effects that can lead to inaccurate results being obtained. Spectral line overlap occurs if matrix components such as other metals absorb light at the same wavelength as the analyte. Fortunately this type of interference is rare because HCL line widths are narrow. If necessary, it can be overcome be chemical separation of analyte and interferent prior to analysis (although this may be time-consuming) or by conducting the measurement at a different analyte wavelength (although this may reduce sensitivity). Interference due to flame emission – the release of light over a range of wavelengths by the hot gases present – can be overcome by modulating the light from the HCL and using a detector that can discriminate between a steady-state and a pulsed signal. Molecular absorption and scattering of light by particles in the flame also occur. These are overcome in commercial AAS instruments by incorporating a background correction system, based on the Zeeman effect or, more usually, a continuum light source such as a deuterium lamp. If the light beams from the D_2 source and the HCL follow exactly the same path through the flame, and each is modulated at a different frequency so that they can be detected individually, then the signal from the HCL represents atomic absorption plus non-specific absorption, whilst the signal from the continuum lamp effectively represents only non-specific absorption. By subtracting one from the other, the corrected absorbance is obtained.

Physical interference effects can arise if the sample and standard solutions are dissimilar in their viscosity or surface tension, and hence are aspirated at different rates. This can usually be overcome by reagent-matching. Chemical interferences can disturb equilibria between analyte molecules and atoms, or between atoms and ions, altering the atomisation efficiency in the sample solution relative to the standard solution (where no matrix is present). Where matrix components form stable compounds with the analyte, fewer atoms are produced (a suppressive interference effect). This may be overcome by addition of a reagent that preferentially binds to the interferent, leaving the analyte free to atomise. The atomisation of Group 1 and Group 2 metals can be affected by the presence of other easily-ionised elements in the sample matrix. If the equilibrium between interferent atoms and ions is strongly in favour of ions, the electrons liberated during ionisation of the interferents will suppress ionisation of the analyte (an enhancing interference effect). Addition of a large excess of a very easily ionised element such as caesium (Cs) to both samples and standards usually overcomes this problem. The analyte can also become physically trapped within particles. Reagents are available, e.g. ammonium chloride and EDTA, that can combat this type of interference effect.

FAAS is a mature analytical technique but still widely applied. It has recently been used to assess the uptake of heavy metals from soil into coffee [49], corn [95], medicinal plants [168] and grapes [204]. The environmental impact of a tannery [200] and a Zn smelter [203] have been assessed, and general differences in metal concentrations in industrial, rural and urban soils studied [229]. One notable recent analytical development is high resolution continuum source FAAS. Although not yet widely used, the technique has provided promising results for the measurement of Cu, Fe, Mn and Zn in 0.005 mol L^{-1} DTPA extracts of agricultural and reference soils [166].

Table 4.4 Typical ETAAS heating programmes[a]

Stage	Temp. (°C) Cd	Temp. (°C) Cr	Duration (s)	Ramp rate (°C s^{-1})	Purpose
Dry	110	110	30	20	Remove solvent e.g. water
Pyrolyse	700	1,650	20	2,000	Remove matrix
Atomise	1,600	2,500	3	>2,000	Generate free analyte atoms
Clean	2,650	2,650	2	>2,000	Remove residue ready for next sample injection

[a] Adapted from [168]

Limits of detection in FAAS are limited to the region of parts-per-million because of the relative inefficiency of sample introduction by pneumatic nebulisation, combined with the short residence time of analyte atoms in the HCL beam and their dilution by the large excess of flame gases present.

4.7.3 Electrothermal Atomic Absorption Spectrometry (ETAAS)

In ETAAS the flame is replaced by an electrically-heated graphite tube atomiser, roughly 3 cm in length and <1 cm in diameter. A small aliquot of analyte solution e.g. 20 μL is pipetted into the tube through a dosing hole in the top and a step-wise heating programme is applied to create analyte atoms. The HCL beam passes along the axis of the tube. Limits of detection are improved greatly relative to FAAS (to around parts-per-billion levels) because the atoms are confined, but chemical interferences are severe, as are memory effects, although the latter can be reduced by use of low permeability, chemically resistant pyrolytic graphite.

The heating programme has to be optimised for each analysis, the goal being to remove as much as possible of the (potentially interfering) sample matrix, but retain the analyte until atomisation.

Examples of furnace programs for measurement of contrasting elements (Cd and Cr) in acid digests are shown in Table 4.4. An inert gas such as N_2 is flowed around and through the furnace, except during atomisation, to protect the tube from combustion and help carry away volatile material. A typical graphite tube might endure several hundred 'firings' before it has to be replaced, but tube lifetime will be reduced substantially if high temperatures are used, or if the sample matrix is corrosive.

Even with an optimised heating cycle, interferences may still persist, notably the formation of volatile analyte species that can be lost during ashing, or of refractory analyte species that do not atomise efficiently. ETAAS is particularly prone to chloride interferences, and these commonly occur when analysing HCl soil digest or $CaCl_2$ soil extracts. A large variety of 'matrix modifiers' – reagents that are added to the furnace together with the sample to improve atomisation – have been developed to overcome interferences in ETAAS. Examples include ammonium nitrate, magnesium nitrate, and palladium nitrate. Another common approach is to delay the atomisation of the sample until the gas within the tube has reached a higher temperature by depositing it not on the tube wall but onto a small graphite platform (called a L'vov platform after its inventor). Further details of interference effects in ETAAS and methods by which these may be overcome can be found in [106].

Nowadays, ETAAS tends to be used in studies where a single element, present at relatively low concentration in soil, is of interest because of its toxicity (recent examples have focussed on Cd [154], Cr [62] and Sb [43]); for the detection of specific chemical species [37], or where ICP-MS is unavailable [31]. A key limitation of both ETAAS and FAAS is that the vast majority of HCLs commercially available contain a single element. This means that atomic absorption spectrometry can measure only one analyte at a time. Whilst there are many situations where only one (or few) heavy metals are of interest, many studies require multi-element analysis.

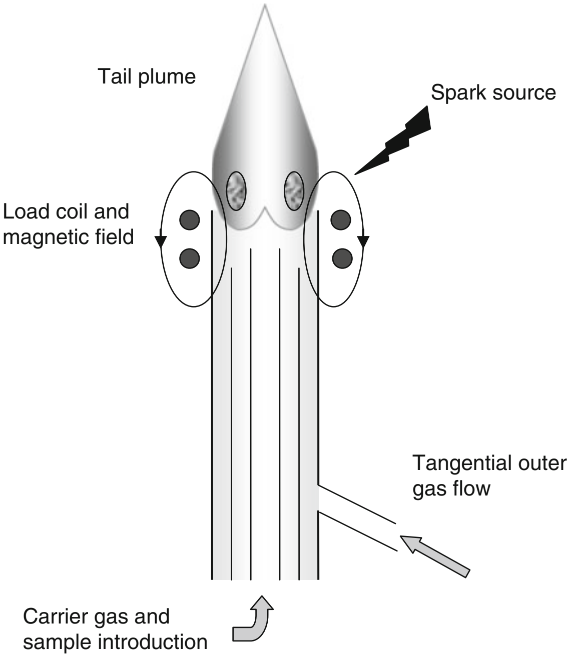
4.7.4 Inductively-Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

Flame atomic emission spectrometry is still used for some specific applications, notably the determination of major cations in soils [168]. The instrumentation is similar to FAAS, except than no HCL is required. However, for most analyses, it has been supplanted by ICP-AES.

Plasma is gas in which a high proportion of the atoms and molecules present have been ionised. Most commercial ICP-AES instrument use an argon plasma operating at a power of 0.5–1.5 kW and a frequency of 27 or 40 MHz. The temperature in the plasma is in the range 7,000–10,000 K (different regions have different temperatures). Hence, there is ample energy available to atomise, excite and even ionise most heavy metals. The argon ICP is formed in a specially designed torch, made of three concentric quartz tubes surrounded by a water-cooled, copper, radio frequency coil (Fig. 4.8). Three streams of argon are supplied. The inner or carrier gas transports the sample aerosol to the ICP, whilst the outer gas helps shape the plasma and prevents it from melting the torch. When radiofrequency energy is supplied to the coil an intense magnetic field is created. Seed electrons generated by a spark from a Tesla coil are accelerated by the field and collide with argon atoms, producing a self-sustaining plasma. The carrier gas punches a hole through the centre of the plasma, giving it a characteristic toroidal shape. Because of the intensity of background spectral emission from the core of the plasma, analytical measurements are usually made in the tail plume, 1–2 cm above the load coil. Even so, significant levels of background emission can reach the detector and so there are significant advantages in viewing the plasma axially, rather than from the side [20].

Soil digests and extracts are introduced to the ICP in a similar way to FAAS. Hence similar physical interference effects can occur. Also as in FAAS, the majority of the sample goes to waste, with just a few percent reaching the plasma. A variety of designs of spray chamber and nebuliser are available [189, 190]. Most routine analysis uses pneumatic or cross-flow nebulisers, but there are also ultrasonic nebulisers (which can increase the proportion of sample entering the

Fig. 4.8 Schematic diagram of an inductively coupled plasma torch



plasma, and hence the sensitivity) and ‘high-solids’ nebulisers. Chemical interferences are effectively eliminated because the energy of the plasma is so much greater than that of a flame that even elements forming refractory oxides are atomised efficiently. In contrast, spectral line overlap is a considerably bigger problem in ICP-AES than in FAAS because the higher temperature environment means that virtually all the elements present in the plasma will have atoms (and ions) in several excited states. When these de-excite a complex spectrum, rich in emission lines, is produced. Separation of the wavelength(s) of interest requires a higher resolution monochromator than in AAS. Echelle spectrometers are most common. These contain two dispersive elements, a grating and a prism. The echelle grating separates light in one direction and the prism in a perpendicular direction. The two-dimensional spectrum produced i.e. a series of short regions of the spectrum, stacked above on another, is focussed onto a charge-coupled device (CCD) detector.

Key advantages of ICP-AES over atomic absorption techniques are the wide dynamic range (several orders of magnitude) and ability to perform multi-element analysis. This means that it is often feasible simultaneously to measure major and trace elements. Since the last edition of this book [3] ICP-AES has become probably the most widely used spectroscopic technique for measuring heavy metals in soils, plants and related materials. Examples of recent applications include the measurement of Ba, Cd, Cu, Fe, Mn, Ni, Pb, V and Ti in urban topsoils [144]; of As, Cd, Cu, Fe, Ni, Pb and Zn in roadside soils [55]; of As, Cd, Cu, Pb and Zn in soils affected by nonferrous metal mining [109] and of Al, Ba, Cr, Cu, Fe, Mn, Ni, Pb, Sr, Ti, V and Zn in peat cores [84]. The technique has also been used to provide insight into phytoremediation of heavy metal contaminated soil using, for example, vetiver grass (*Chrysopogon zizanoides*) [8] and to study the input of heavy metals to soil from application of fertilizers [131].

The main limitation of ICP-AES is that the LOD achievable – typically parts-per-million levels or a little lower – are insufficient for some applications. For example, when measuring phytoavailability by application of a neutral salt solution to a relatively uncontaminated soil, the concentrations of heavy metal released may be too low for accurate measurement. This problem can be overcome by coupling the ICP to a mass spectrometer.

4.7.5 Inductively-Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS is the newest atomic spectrometry technique to become widely applied in soil analysis. Relatively rare 20 years ago because of high instrument cost and the need for a specialist, skilled operator, it is now frequently used in multi-element studies of heavy metal distribution in relation to potential pollution sources e.g. [121, 151, 233] and in work focused on trace element uptake by plants [181] or biogeochemical cycling [194].

The ICP is the same as that in AES but, instead of measuring light emitted, the ions generated in the plasma are directed into a quadrupole mass analyser (typically capable of unit mass resolution i.e. discrimination of m from $m - 1$ or $m + 1$). One of the major challenges in developing ICP-MS was extracting ions from the hot, dense plasma into the high vacuum environment of the mass analyser. Modern instrument interfaces use two, water-cooled nickel or platinum cones for this purpose (Fig. 4.9). The first cone is positioned in the tail plume of the plasma and allows an expanding jet of material to pass through its ~1.0 mm orifice into an intermediate vacuum region. The second, 'skimmer', cone sub-samples this jet, allowing a small proportion of the ions into a higher vacuum region where they are accelerated into the quadrupole.

ICP-MS has LOD similar to those of ETAAS (parts-per-billion or lower) but the capability to perform multi-element and isotopic analysis. Common interferences include deposition of solid material at the tip of the cones, especially when analysing sample solutions containing high concentrations of dissolved solids. This can be overcome by sample dilution, but with a concomitant reduction in LOD. More important are the occurrence of isobaric interference (e.g. that of ^{40}Ar on the measurement of ^{40}Ca) and of polyatomic ions from the plasma or sample matrix at the same mass to charge ratio as the analyte ion. These can sometimes be removed by changing the sample preparation procedure e.g. the interference of $ArCl^+$ on As^+ at m/z 75 may be avoided by use of nitric acid rather than *aqua regia* in soil digestion, but interferences arising from the plasma itself are more difficult to overcome e.g. that of Ar_2^+ on Se^+ at m/z 80. One option is to use a different analyte isotope for quantification, but this will lead to a reduction in sensitivity if the relative abundance is lower than that of the original isotope, and it is impossible for mono-isotopic elements such as As. The newest generation of commercial ICP-MS instruments incorporate devices to overcome polyatomic ion interference. Different manufacturers approach

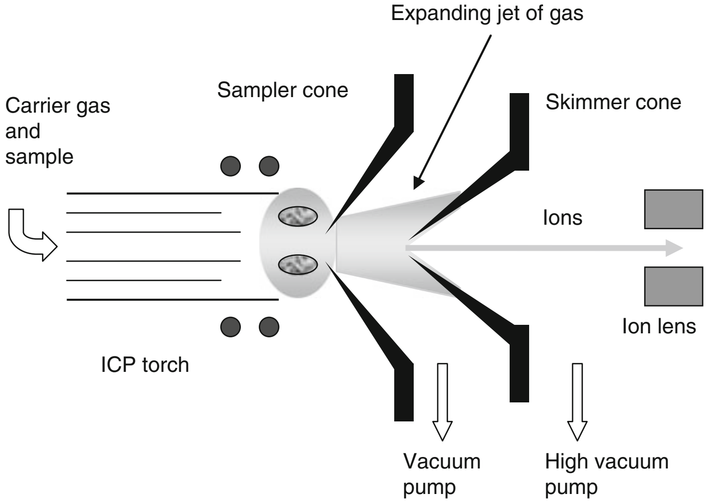


Fig. 4.9 Schematic diagram of an ICP-MS interface

the problem slightly differently. Options include the breaking-up of the interfering ions into their component atoms, altering their mass through reaction with reagent gas (e.g. H_2) or changing their energy through collisions with inert species (e.g. He). The overall effect is to free the analyte ion for detection.

An alternative approach is to replace the quadrupole mass analyser with a magnetic sector. Sector field-ICP-MS offers many analytical advantages, including excellent mass resolution [101] – indeed the technique is sometimes called high resolution-ICP-MS – but significantly increases the cost of the instrument. It tends therefore to be used for rather specialist applications such as the accurate measurement of stable isotope ratios [157, 193].

There is considerable interest in the development and use of various sample introduction systems for ICP-MS and/or ICP-AES. Approaches currently being explored include electrothermal vaporisation [79, 170, 206], laser ablation (see Sect. 4.4.4) and the direct coupling of chromatography with ICP-MS [81] for speciation analysis (see Sect. 4.8).

4.7.6 *Other Types of Atomic Spectrometry*

Hydride generation atomic absorption spectrometry (HGAAS) is applicable to the elements As, Bi, Ge, Pb, Sb, Se, Sn and Te, all of which form volatile hydrides on reduction with sodium borohydride in acid media. The hydrides are swept into an atom cell where they are decomposed to atomic vapour. The cell is usually a quartz glass tube. It may be electrically heated or placed in the flame of an FAAS instrument. The main advantage of hydride generation methods is increased sensitivity relative to conventional solution nebulisation. A limitation is that the technique suffers from chemical interference effects, especially due to the presence of transition metals such as nickel, which can affect the hydride generation efficiency in solution. Recent applications include the measurement of Pb in soil digests [120] and several studies involving sequential extraction of Se [21, 110]. Petrov et al. [155] recently described an optimised method for As speciation in EDTA extracts of soil and sediment by continuous flow-HGAAS.

Cold vapour atomic absorption spectrometry (CVAAS) is used to measure Hg in soil [211]. Monatomic elemental Hg vapour is generated from sample extracts or digests by reduction, usually with tin(II) chloride, and swept into the light beam from a hollow cathode lamp. No heating of the atom cell is required. Sensitivity can be improved by preconcentration on gold amalgam [70]. CVAAS methods are available to allow separate measurement of inorganic and organic Hg species [205].

In atomic fluorescence electrons are promoted by photons and the light emitted when they return to their ground states ('fluoresce') is measured. In atomic fluorescence spectrometry (AFS) a plasma source may be used to atomise the sample, but excitation of the atoms is brought about by an element-specific EDL or by a tunable laser [64, 223]. AFS is potentially a powerful analytical technique, combining some of the advantages of AAS and AES. However, current applications are relatively limited, tending to focus on the measurement or speciation of hydride-forming elements such as As [48, 175, 231], Sb [43] and Se [232] or on the determination of Hg by cold vapour AFS [66, 78].

4.7.7 Other Analytical Techniques

Although the measurement of heavy metals in soils is dominated by atomic (and elemental mass) spectrometry, other techniques are used. There are developments and applications of capillary electrophoresis [2, 65, 213], ion chromatography [191], ion-selective electrodes [44] and stripping voltammetry [1]. Electroanalytical instruments can be made that are capable of rapid, sensitive, selective analysis [56, 72] and there is strong interest in developing hand-held systems e.g. for field speciation of As [126].

4.8 Speciation and Speciation Analysis

Speciation refers to the chemical 'form' of an analyte e.g., its oxidations state, the atoms or molecules it is bound to, or mineral phases with which it is associated. Ure [208] subdivided speciation into three classes:

(i) classical speciation, where a specified chemical form is considered e.g., $\mathrm{Cr^{III}}$ *vs*. $\mathrm{Cr^{VI}}$ or inorganic mercury *vs*. monomethylmercury
(ii) functional speciation, where species are defined by their role e.g., plant-available species

(iii) operational speciation, where species are defined by the reagents used to extract them e.g., 0.05 mol L^{-1} EDTA-soluble species, or metals released by a sequential extraction.

More recently, IUPAC adopted a narrower definition [201] similar to the 'classical' speciation of Ure. This latter definition is the one used in this chapter.

Speciation is a key factor influencing the mobility, fate, bioavailability and toxicity of heavy metals in soils. Potentially toxic elements for which speciation is currently of particular interest include As, Cr, Hg, Pb, Sb, Se and Sn, many of which form environmentally-important organometallic species. Speciation analysis (measurement of the kinds and amount of heavy metal species present) is an extremely challenging, but rapidly expanding, area of analytical science [35, 57, 74].

As noted in 4.4.2, direct speciation analysis of metals and metalloids in soils is now possible with synchrotron-based X-ray techniques. In recent examples, extended X-ray absorption fine structure (EXAFS) spectroscopy has been used to measure Pb species in soil and assess the effectiveness of phosphate-induced immobilisation [76], whilst X-ray absorption near edge structure (XANES) revealed information on the mechanism of transport of Cu and Mn across the soil/root interface [140] and on transformation of Cr^{VI} to Cr^{III} in soil [93]. Voegelin et al. [216] used several X-ray techniques to study As in riparian floodplan soils. Synchrotron micro-XRF showed the distribution of As closely matched that of Fe in the vicinity of plant roots; XANES showed the As was mainly present as As^{V}, and EXAFS confirmed an association between As and iron (oxy)hydroxide species. A similar association of Sb^{V} with iron minerals was found in soil from a shooting range in Switzerland [185].

Other approaches for speciation of heavy metals in soils are based around the coupling of chromatographic separation methods to element-specific detectors such as ICP-MS. Great care must be taken during sample pretreatment since there is considerable danger of altering the original speciation, in which case the results obtained will lose their environmental relevance.

Size exclusion chromatography-ICP-MS has revealed associations between heavy metals and different forms of dissolved organic matter in soil solution [199] and leachates [105]. Analysis by high performance liquid chromatography-ICP-MS showed that little of the Hg present in a contaminated soil was present in the soil solution and available for plant uptake [30]. Measurement of methylated species of As, Sb and Sn in urban soils by hydride generation gas chromatography followed by ICP-MS has improved understanding of the biogeochemical cycling of these elements [51].

4.9 Quality Assurance

Laboratories involved in the determination of heavy metals in soils, whether for regulatory or research purposes, should regularly monitor the quality of their analyses [5]. A range of approaches are available. At the very least, appropriate blanks should be analysed (both reagent and procedural blanks) to check for contamination, whilst analysis of replicate test portions will provide an indication of the repeatability and precisions of measurement.

A Certified Reference Material (CRM) is a soil or other material in which one or more metal concentrations have been firmly established, through analysis by several laboratories using a range of analytical techniques. Results are subject to keen scrutiny and only those in which there is a high degree of confidence are accepted as certified values [160, 161]. CRMs are prepared and issued by agencies such as NIST in the USA and JRC-Ispra in Europe [138]. They are available for a variety of soil types and analytes (see Table 4.5). When using a CRM, it is important to select one as similar as possible in composition to the samples and certified for the type of extraction being performed. CRMs can be used to assess the accuracy of a new analytical method or instrument, to establish whether results of an established method are under control, and as an aid in training or monitoring the competence of staff. Limitations of CRMs include their high cost and the fact that they are available for a restricted range of soil types, analytes and extraction procedures. As a consequence, many laboratories prepare their own, in-house, reference materials (RM). These are soils, often with characteristics relevant to a particular study (e.g. urban soils [40]) which are obtained, homogenised, stabilised (e.g. by heat treatment) and their heavy metal contents established by analysis of replicate test-portions in parallel with CRM and, if possible, by more than one laboratory. The RM can then be incorporated into all batches of analysis and control charts plotted to monitor the long-term reproducibility of the analytical method, whilst the CRM is included only periodically to ensure accuracy is maintained.

Another way in which trace metal laboratories can assess their competence is to participate in inter-comparison exercises (also called proficiency tests) [152, 230]. These are organised by various national and international bodies and involve the distribution for analysis of test samples whose composition is usually known to the organisers but not to the recipients. Alternatively, laboratories working together may elect to exchange check-samples for analysis [40]. Proficiency tests are particularly useful in identifying bias in particular laboratories or methods.

Inter-laboratory harmonisation can also be enhanced by using standard analytical methods [22], especially those recommended by national bodies such as the USEPA (United States), BSI (UK) and DIN (Germany), and by the International Organisation for Standardisation (ISO). Advantages of these are that they are well-established and thoroughly tested methods, and hence results obtained by different laboratories should be comparable. A disadvantage is that it takes a considerable amount of time and discussion for the international soil science community to agree on a standard method. Hence, their availability tends to lag behind advances in analytical science. A selection of current ISO methods relevant to the measurement of heavy metals in soils is provided in Table 4.6. However, new guidelines are continually being produced. For the most up-to-date list, the reader is directed to the ISO website, www.iso.org/iso/home.htm

Table 4.5 A selection of soil certified reference materials

CRM	Material	Extraction	Analytes[a]
SRM 2709a	San Joaquin soil (uncontaminated)	Total	Al, Ba, Ca, Cd, Cr, Co, Fe, K, Mg, Mn, Na, P, Pb, Sb, Si, Sr, Ti, V, Zn
SRM 2710a	Montana I Soil (highly contaminated)	Total	Al, As, Ba, Ca, Cd, Co, Cu, Fe, Hg, K, La, Mg, Mn, Na, P, Pb, Sb, Si, Sr, Ti, U, Zn
SRM 2711a	Montana II Soil (slightly contaminated)	Total	Al, As, Ba, Ca, Cd, Cr, Co, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, P, Pb, Si, Sb, Sm, Sr, Ti, U, V, Zn
SRM 2586	Soil contaminated with Pb from paint	Total	As, Cd, Cr, Pb (nominally 500 mg kg^{-1} Pb)
SRM 2587	Soil contaminated with Pb from paint	Total	As, Cd, Cr, Pb (nominally 3,000 mg kg^{-1} Pb)
SRM 2701	Hexavalent chromium in soil	Total and EPA method 3060A	Total Cr, Fe, Mn; method 3060 extractable Cr(VI);
SRM 4353	Rocky Flats soil number 2	Total	Radionuclides
BCR-142R	Light sandy soil	Total	Cd, Co, Cu, Hg, Mn, Ni, Pb, Zn
		Aqua regia	Cd, Co, Cu, Mn, Ni, Pb, Zn
BCR-143R	Sewage sludge amended soil	Total	Cd, Co, Cu, Hg, Mn, Ni, Pb, Zn
		Aqua regia	Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn
ERM-CC690	Calcareous soil	Total	Ce, Dy, Gd, La, Nd, Sc, Sm, Tb, Th, Tm, U, Yb
BCR-483	Sewage sludge amended soil	EDTA, acetic acid, calcium chloride, sodium nitrate, ammonium nitrate	Cd, Cr, Cu, Ni, Pb, Zn
BCR-484	Sewage sludge amended (terra rossa) soil	EDTA, acetic acid	Cd, Cu, Ni, Pb, Zn
BCR-700	Organic-rich soil	EDTA, acetic acid	Cd, Cr, Cu, Ni, Pb, Zn
BCR-701[b]	Lake sediment	BCR sequential extraction	Cd, Cr, Cu, Ni, Pb, Zn

[a] Not all analytes are certified – some may have indicative values only – and so it is advisable to check with the supplier before purchasing a CRM

[b] Although not a soil, this is the only CRM available certified for metals extractable by sequential extraction and so is often used by soil trace metal laboratories

Table 4.6 A selection of ISO methods relevant to heavy metals in soil

Method	Title
ISO 10381–1:2002	Soil quality – Sampling – Part 1: Guidance on the design of sampling programmes
ISO 10381–2:2002	Soil quality – Sampling – Part 2: Guidance on sampling techniques
ISO 10381–3:2001	Soil quality – Sampling – Part 3: Guidance on safety
ISO 10381–4:2003	Soil quality – Sampling – Part 4: Guidance on the procedure for the investigation of natural, near-natural and cultivated sites
ISO 10381–5:2005	Soil quality – Sampling – Part 5: Guidance on the procedure for the investigation of urban and industrial sites with regard to soil contamination
ISO 11047:1998	Soil quality – Determination of Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn – Flame and electrothermal atomic absorption spectrometric methods
ISO 11464:2006	Soil quality – Pretreatment of samples for physico-chemical analysis
ISO 11466:1995	Soil quality – Extraction of trace elements soluble in aqua regia
ISO 14869–1:2001	Soil quality – Dissolution for the determination of total element content – Part 1: Dissolution with hydrofluoric and perchloric acids
ISO 14869–2:2002	Soil quality – Dissolution for the determination of total element content – Part 2: Dissolution by alkaline fusion
ISO 14870:2001	Soil quality – Extraction of trace elements by buffered DTPA solution
ISO 15903:2002	Soil quality – Format for recording soil and site information
ISO 16772:2004	Soil quality – Determination of Hg in aqua regia soil extracts with cold-vapour atomic spectrometry or cold-vapour atomic fluorescence spectrometry
ISO/TS 17924:2007	Soil quality – Assessment of human exposure from ingestion of soil and soil material – Guidance on the application and selection of physiologically based extraction methods for the estimation of the human bioaccessibility/bioavailability of metals in soils
ISO 18512:2007	Soil quality – Guidance on long and short term storage of soil samples
ISO 19730:2008	Soil quality – Extraction of trace elements from soil using ammonium nitrate solution
ISO 20279:2005	Soil quality – Extraction of Tl and determination by electrothermal atomic absorption spectrometry
ISO 20280:2007	Soil quality – Determination of As, Sb and Se in aqua regia soil extracts with electrothermal or hydride generation atomic absorption spectrometry
ISO 22036:2008	Soil quality – Determination of trace elements in extracts of soil by inductively coupled plasma atomic emission spectrometry (ICP-AES)
ISO 23909:2008	Soil quality – Preparation of laboratory samples from larger samples
ISO 25177:2008	Soil quality – Field soil description

Finally, laboratories conducting commercial soil analysis for regulatory, legislative or forensic purposes may seek accreditation of their analytical procedures from relevant national bodies e.g. the United Kingdom Accreditation Service (UKAS) for British laboratories. UKAS accredited laboratories must demonstrate high levels of analytical traceability and pass rigorous inspection visits by teams of expert assessors.

Table 4.7 Key characteristics of some atomic spectrometry techniques

Technique	Single or multi-element analysis	Sample form	Portable version available	Relative cost to purchase
INAA	Multi	Any	No	–
XRF	Multi	Solid	Yes	High (for a lab based instrument)
LIBS	Multi	Solid	Yes	–
LA-ICP-MS	Multi	Solid	No	Very high
FAAS	Single	Liquid	No	Low
ETAAS	Single	Liquid	No	Moderate
ICP-AES	Multi	Liquid	No	Moderate
ICP-MS[a]	Multi	Liquid	No	High
ICP-MS[b]	Multi	Liquid	No	Very high

[a] Quadrupole mass analyser
[b] Magnetic sector mass analyser

4.10 Concluding Comments

Although a variety of other approaches are used, the determination of heavy metals in soils is still performed chiefly by spectrometry, with different techniques used, depending on their capabilities (Table 4.7). As was predicted a decade ago [195] multi-element methods based on ICP-AES and ICP-MS are now predominant, although FAAS (often with analyte preconcentration) is still widely used, as is ETAAS for specific applications. Techniques formerly the exclusive provenance of research laboratories e.g. LA-ICP-MS and LIBS, are now finding wider application. Speciation analysis remains of interest, with applications of direct methods for the determination and speciation of heavy metals in soils increasing. To keep up with current developments in spectroscopic methods for measurement of heavy metals in soils, the reader is directed to the Atomic Spectrometry Update on Environmental Analysis, published annually in the *Journal of Analytical Atomic Spectrometry* e.g. see [23, 24].

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