



Environment Agency

The determination of metals in solid environmental samples (2006)

Methods for the Examination of Waters and Associated Materials

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This booklet contains guidance on the determination of metals in solid environmental samples using a variety of techniques. Using the procedures described in this booklet should enable laboratories to satisfy the relevant requirements of the Agency's Monitoring Certification Scheme (MCERTS) for laboratories undertaking chemical testing of soils⁽¹⁾. However, if appropriate, laboratories should clearly demonstrate they are able to meet the MCERTS requirements. Each method has been validated in only one laboratory and consequently details are included for information purposes only as an example of the type of procedures that are available to analysts. Information on routine multi-laboratory use of these methods would be welcomed to assess their full capabilities. Each method has been accredited by UKAS and conforms to the MCERTS performance standard for laboratories undertaking chemical testing of soil, meeting the performance criteria prescribed therein for a selection of metals.

Whilst this booklet may report details of the materials actually used, this does not constitute an endorsement of these products but serves only as an illustrative example. Equivalent products are available and it should be understood that the performance characteristics of the method might differ when other materials are used. It is left to users to evaluate methods in their own laboratories.

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About this series

Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, waste water and effluents as well as sewage sludges, sediments, soil (including contaminated land) and biota. In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection. Often, full evaluation is not possible and only limited performance data may be available.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

Standing Committee of Analysts

The preparation of booklets within the series "Methods for the Examination of Waters and Associated Materials"

and their continuing revision is the responsibility of the Standing Committee of Analysts. This committee was established in 1972 by the Department of the Environment and is now managed by the Environment Agency. At present, there are nine working groups, each responsible for one section or aspect of water quality analysis. They are

- 1 General principles of sampling and accuracy of results
- 2 Microbiological methods
- 3 Empirical and physical methods
- 4 Metals and metalloids
- 5 General non-metallic substances
- 6 Organic impurities
- 7 Biological methods
- 8 Biodegradability and inhibition methods
- 9 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with these methods are listed at the back of the booklet.

Publication of new or revised booklets will be notified to the technical press. If users wish to receive copies or advance notice of forthcoming publications, or obtain details of the index of methods then contact the Secretary on the Agency's internet web-site (www.environment-agency.gov.uk/nls) or by post.

Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary.

Dr D Westwood
Secretary
June 2005

Warning to users

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc Act 1974 and regulations made under this Act, and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is

noted. Numerous publications are available giving practical details on first aid and laboratory safety. These should be consulted and be readily accessible to all analysts. Amongst such publications are; "Safe Practices in Chemical Laboratories" and "Hazards in the Chemical Laboratory", 1992, produced by the Royal Society of Chemistry; "Guidelines for Microbiological Safety", 1986, Portland Press, Colchester, produced by Member Societies of the Microbiological Consultative Committee; and "Safety Precautions, Notes for Guidance" produced by the Public Health Laboratory Service. Another useful publication is "Good Laboratory Practice" produced by the Department of Health.

Glossary

AAS	atomic absorption spectrometry
<i>aqua regia</i>	This is normally a 3:1 v/v mixture of concentrated hydrochloric acid and concentrated nitric acid
AFS	atomic fluorescence spectrometry
AQC	analytical quality control
CRM	certified reference material
EDTA	ethylenediamine tetraacetic acid
ETAAS	electrothermal atomic absorption spectrometry (see also GF-AAS)
GF-AAS	graphite furnace atomic absorption spectrometry (see also ETAAS)
ICP-AES	inductively coupled plasma-atomic emission spectrometry, see ICP-OES
ICP-MS	inductively coupled plasma-mass spectrometry
ICP-OES	inductively coupled plasma-optical emission spectrometry
LOD	limit of detection
MCERTS	The Environment Agency's Monitoring Certification Scheme
psi	pounds per square inch
rf	radio frequency
RSD	relative standard deviation
SG	specific gravity
SGV	soil guideline value
UKAS	United Kingdom Accreditation Service
XRF	x-ray fluorescence

The determination of metals in solid environmental samples

1 Introduction

Many metallic species are known to exert toxic effects on biological organisms and many traditional industrial processes have in the past had an adverse effect on local environments. Clearly, the non-degradable nature of metallic species coupled with their tendency to bind strongly with soil material can lead to long term contamination. Knowledge of the metal content of soils is thus important for assessing potential contamination. Guidance, in the form of soil guideline values (SGVs) has been produced and is being developed⁽²⁾ to inform assessors on the risks from environmental contamination. This booklet describes ten methods for the determination of certain metals in soils, which may also be applicable to, or adapted for, sediments and sludges.

The determination of metals in solid environmental samples is a challenging process for many laboratories and depends on many factors including sample preparation and pre-treatment, extraction and digestion strategy and end detection technique. Generally, the analysis of a solid environmental matrix for metal determination requires the preparation of a dried, ground, homogeneous material and extraction or digestion of this material with concentrated acid or acid mixture at elevated temperatures. To accomplish this, a variety of procedures are available.

1.1 Sample pre-treatment and preparation

The preparation and pre-treatment of soils prior to chemical analysis is a major consideration in the generation of reliable data. Notwithstanding the quality of the subsequent analysis, if an inappropriate sample has been taken and/or an associated sub-sample has been incorrectly prepared, then the results generated from that sub-sample will be of little value. Furthermore, it will be impossible to offer decisive or definitive interpretations to these results. Further details are given elsewhere in this series⁽³⁾.

1.2 Extraction and digestion

The extraction or digestion of the pre-treated and prepared sample can be carried out using a variety of solution mixtures in open or closed vessels, and the energy source provided by a range of techniques, for example, hot-plate or micro-wave systems. When determining metallic concentrations in soils, the extraction or digestion procedure is often the main source of variation associated with determining the true (i.e. total or absolute) concentration present in a sample. This variability can be significant. Further guidance on this, based on the comparison of results obtained using four methods for the determination of a variety of metals in three solid environmental samples, can be found elsewhere⁽⁴⁾. In particular, low results can occur for certain metals in certain matrices due to the precipitation of metallic insoluble salts or losses from open extraction vessels. Additionally, constituents of the sample matrix can influence the extraction or digestion process, and consequently the concentrations of metals determined. This is a particular problem for samples containing large amounts of silica-based constituents. Such samples require vigorous conditions for the complete extraction of the metal from the crystal lattice or digestion of the sample matrix.

There is, therefore, a need to develop a range of methods which give optimum performance for a range of metals in a variety of matrices but which possess the required level of accuracy⁽¹⁾. It is almost certain that no single method will achieve comparable

performance for all metals in a variety of matrices. Hence, it is more appropriate to use a variety of extraction and digestion procedures, each of which give optimum performance for a specific metallic element in a specific type of matrix. Whilst this approach is more costly, it does enable results to be generated that are more accurate and reliable, and hence greater confidence can be placed on the values reported.

1.3 Detection techniques

When extraction or digestion is deemed complete, the concentration of the metallic species in the resulting solution can then be determined using an appropriate end detection technique, and ICP-OES, ICP-MS, ETAAS, AFS, AAS and cold vapour/hydride generation techniques have been shown to be suitable. Guidance on these procedures and techniques has previously been published within this series^(5 - 14). Various end detection techniques may be used for the final quantification stage and these techniques play a major part in achieving optimum performance. However, care should be taken that interference effects relating to or impinging on the quantification stage do not cause significant errors. Analysts wishing to determine a variety of metals or use specific techniques of quantification should evaluate their procedures thoroughly before use.

1.4 Matrix

The underlying analytical problem with soil analysis is that soils are complex mixtures of organic and inorganic substances. These substances need to be broken down completely to afford total dissolution of the metal species. Hence, a variety of extraction and digestion procedures need to be developed to optimise the extraction of selected metal species from the matrix. The more severe or extreme the extraction or digestion procedure, the more likely that complete extraction (i.e. 100% recovery) of the metal species from the matrix will occur. Strongly oxidising, very acidic solutions are more likely to afford complete extraction.

The extractability of metal from soil depends on the form in which the metal species is present and whether the metal species is bound to the soil matrix. Where samples are spiked simply by mixing the matrix with either the metal species or a compound of the metal species, then this procedure may not enable a true estimate of the metal content to be determined, i.e. 100% recovery may not be achieved.

The efficiency of extraction may be checked by examining any residue left after extraction or digestion, or by collecting and analysing fumes given off to ascertain whether any loss of volatile metal species occur. The analysis of any insoluble residues may entail the use of solid sample analytical methods such as XRF techniques or for example, hydrofluoric acid digestion procedures may be employed for determining metals in insoluble residues.

For a thorough investigation of the extraction or digestion stage, samples of known composition are available and should be analysed using the entire method, including the end detection technique. Matrix certified reference materials are available for this purpose. However, when a certified reference material is used care should be taken to ensure the result determined by the method used reflects the CRM value and the method or methods used to determine the CRM value. If not, it may be observed that “like for like” values are not being compared. For example, if a total metal concentration is reported for a particular CRM and an extraction procedure is used to determine a particular metal concentration that results in less than 100% recovery, then a negative bias will always be recorded, the magnitude of which will depend on the recovery.

2 Extraction and digestion procedures

A wide variety of acid mixtures have been used to extract or digest solid environmental samples and it is rare for only one acid to be used in the extraction or digestion of sample matrices. Examples of extraction solutions that have been used to determine metal concentrations in soils include water, EDTA solutions, acetic acid solutions, concentrated nitric acid and *aqua regia*. In addition, different hydrochloric and nitric acid ratios have been used. Examples of digest solutions include mixtures of nitric, hydrochloric and hydrofluoric acids, or mixtures of nitric and perchloric acids. Occasionally, it may be necessary to use fusion techniques to afford complete dissolution or digestion of the sample matrix. For example fluxes might include lithium metaborate, sodium carbonate, and sodium peroxide. The use of fluxes may considerably increase problems with matrix effects and/or interferences with ICP-OES. Additionally, the high level of dissolved solids caused by such fluxes may preclude the use of certain end detection techniques due to the high levels of dilution required to bring the level of dissolved solids to within an acceptable range. The choice and strength of acid mixture is dependent on the sample matrix, metal species being determined and the end detection technique employed. For example, with hydrochloric acid, volatile chlorides may be produced (notably chlorides of mercury, arsenic, antimony and selenium). With other acids, insoluble metal salts may be formed. Depending on the end detection technique employed, it may be necessary to add matrix modifiers to the final solution. For example, if molybdenum is to be determined by AAS, ammonium perchlorate solution may need to be added to overcome interferences caused by the presence of calcium. For other metal species, it may be necessary, to add potassium, caesium or lanthanum chloride solution to suppress ionisation of a specific element.

Most procedures involving an extraction process (and some procedures involving a digestion stage) will not enable the total (true) metal concentration to be determined. Only complete dissolution of the sample matrix will ensure the total concentration can be determined. The degree to which most metal species are extracted and approach 100 % recovery will depend on many factors including the choice and strength of the acid mixture used, the temperature and duration of the extraction or digestion process and possibly, the end detection technique employed. Whilst not easily explained, “memory” effects may also play a significant role.

In some instances, it may be necessary to consider pre-treatment of the sample before sample extraction or digestion takes place. For example, in the case where samples are contaminated with spent oxide waste material, pre-treatment of the sample with ammonium hydroxide solution⁽¹⁵⁾ before acid extraction has shown that significantly increased recoveries are produced for copper and nickel, compared with results determined without a pre-treatment stage. Since it is rarely known to what extent samples may be contaminated with waste material, such as spent oxide, consideration should be given to including pre-treatment procedures, appropriate to suspected matrix contamination like for example spent oxide, before commencing extraction or digestion.

3 End detection techniques

As already pointed out a variety of end detection techniques may be suitable for determining metal concentrations in soils. More recently, the use of ICP-MS and ICP-OES has become more popular as technology improves, and the use of techniques such as AAS and ETAAS less common. All techniques suffer to some degree interferences caused by spectral and/or matrix (i.e. chemical) factors. The progression towards hotter flames, for

example from air/acetylene and nitrous oxide/acetylene flames to argon plasmas has generally lead to a reduction in potential chemical interferences but not their total elimination. Procedures that may need to be considered to deal with chemical interferences include matrix matching of the calibration standard solutions or the use of standard addition techniques, the use of matrix modifiers or the physical separation or extraction of the specific metal species of interest. Physical characteristics such as viscosity, surface tension, dissolved solids content, etc may also contribute towards matrix matching problems.

Generally, ICP-OES exhibits inferior limits of detection compared to ICP-MS and ETAAS and it is well documented that precision deteriorates as the concentration approaches the limit of detection value. For most metallic species, alternative wavelengths are available with ICP-OES techniques for determining concentrations, and it may be necessary to investigate the choice of wavelength for specific metals as different results may be generated based solely on which wavelength is used. The presence of a metal at a high concentration but possessing a low intensity wavelength may cause severe interferences with a metal present at a low concentration but possessing a high intensity wavelength. For most metals it should be possible to identify a particular wavelength where interferences are minimised. For example, in a recent study⁽⁴⁾ of three chromium wavelengths, the wavelength at 267.7 nm gave highest recoveries, whilst at 357.8 nm, lower recoveries were always observed. Similarly, of two copper wavelengths studied, the wavelength at 327.3 nm always gave higher recoveries than the wavelength at 324.7 nm. Where high concentrations are known or suspected it may be appropriate to choose a weaker or low intensity wavelength. This approach may also negate the need to make excessive dilutions of the extracted or digested solution. Where interference correction factors are used, it may be necessary for these factors to be checked over their entire range of application. For example, when two very large interference factors are used and these need to be subtracted to produce a very small number, significant errors may arise in the number generated, leading to greater variability. Additionally, where there is a change in the plasma conditions, for example, change of argon flow, replacement of torch, etc, interference correction factors may need to be checked to ascertain if they are still appropriate. Table 1 highlights possible interferences using ICP-OES for certain metal species. Wavelengths other than those shown may be used, and individual choices will depend on the type of instrument used and how it is set up (for example axial or radial orientation) and on the matrix of the sample. Other interferences may be present and the list is not exhaustive.

Similar arguments can also be developed for ICP-MS where alternative isotopic masses can be used to monitor metal species. In this case, the natural abundance of the isotopic mass may also play an important role on the results generated. For example, for high metal concentrations it may be more appropriate to use an isotopic mass from a metal species with a naturally low abundance. Spectral interferences observed in ICP-MS can be divided into two categories, namely isobaric interferences and polyatomic interferences. Isobaric interferences arise when the isotopic mass of a metal species overlaps with the mass of another element. For example the isotope ^{116}Sn overlaps with ^{116}Cd . Polyatomic interferences arise when molecular ions are formed in the plasma. These ions originate from the gases used in the instrument (for example argon) and from the reagents used for the extraction or digestion stages. In addition, these ions also originate from the sample matrix and consequently will differ from sample to sample. Where isotopic correction equations are used, it may be necessary to check the range of interferent concentrations where the isotopic correction equations remain valid. Table 2 highlights possible interferences using ICP-MS for certain metal species. However, the effect of the

interference on an isotope will depend on the type of instrument used and how it is set up, as well as on the matrix. Other interferences may be present and the list is not exhaustive.

Hence the choice of wavelength or isotopic mass used to monitor the metal species is an important consideration for ensuring results are obtained that are representative of the true concentration. In some cases, interferences can result in values being determined that are much greater than the actual concentration, or indeed much less. Ideally, some knowledge of the major constituents of the sample is required so that likely interferences can be identified and the appropriate wavelength or isotopic mass chosen to monitor the metal species. If this information is not available then it may be appropriate to monitor several wavelengths or isotopic masses of the specific metal species. However, reducing the effect of interferences requires method development and optimisation of procedures on a metal by metal basis and on a matrix by matrix basis.

When deciding on the most appropriate end detection technique to use, the need for the analysis and the end-use of the results should be taken into consideration. Where different end detection techniques are used and different results are generated, this may not be a problem in that the same conclusions may be reached. However, where it is more critical and the comparability of results from different end detection techniques becomes more of an issue, then greater accuracy is required to make a more meaningful decision. Hence it may be more appropriate in these cases to use the end detection technique that produces greater accuracy. In these cases, it may be more appropriate to use more traditional methods for example, hydride generation techniques for metals such as arsenic and selenium, and for mercury, cold mercury vapour determinations using fluorescence detection.

4 Tolerances

In the procedures described in this booklet any reference to the tolerances to be adopted with respect to time or the amount or volume of reagents etc to be used is left to the discretion of the laboratory. These tolerances should be as low as possible in order to satisfy stringent performance criteria as prescribed, for example in the MCERTS performance standard for laboratories undertaking chemical testing of soil⁽¹⁾. Tolerances of between 1 - 5 % have been shown to be satisfactory.

5 Calibration/AQC solutions

Calibration and other AQC, independent or check calibration solutions should be prepared from reagents from different suppliers, or if the same supplier cannot be avoided, from different batch numbers. AQC, independent or check calibration solutions provide an independent check on the calibrations.

Table 1 Possible interferences for certain metal species with ICP-OES

Element	Wavelength (nm)	Possible interferences
aluminium	308.215	Mn (308.205), V (308.211)
	396.152	Mo (396.151), Fe (396.114)
antimony	206.834	Cr (206.839)
	217.581	Fe (217.545)
arsenic	189.042	Cr (188.992)
	193.696	Fe (193.663)
barium	455.403	Cs (455.531)
beryllium	313.042	V (313.027)
cadmium	214.440	Fe (214.445)
	226.502	Fe (226.505), Co (226.487), Ti (226.512)
	228.802	Co (228.781), As (228.812)
chromium	361.051###	Fe* (361.016), Ti* (361.016), Mn* (361.030), Ni* (361.046)
	267.716	Mn (267.725), Mo (267.699), V (267.730 and 267.780)
	283.563	Fe* (283.570 and 283.455), Mo (283.535 and 283.553)
	284.325	Fe (284.324 and 284.359)
cobalt	357.869	V (357.864), Co (357.890), Fe (357.838)
	228.616	Ti (228.618), Cr (228.627), Ni (228.615)
	230.786	Mo (230.798), Ni (230.779)
copper	236.380	Fe* (236.387), Cr (236.401)
	238.892	Fe* (238.863 and 238.895), V (238.892)
	224.700	Pb* (224.689), Mo (224.695), Fe (224.691), Ni (224.723)
	324.752	Mo (324.762), Co (324.718), Fe (324.717)
iron	327.393	Co (327.393), Ti (327.405)
	259.940	Mo (259.918)
	238.204	Co (238.232, 238.176)
lead	239.562	Co (239.551)
	217.000	Fe* (216.992), Al* (216.988), Sb (217.017), Mo (217.015), Ni (216.992), V (217.007)
manganese	220.350	Ti (220.367), Co (220.343), Mo (220.336 and 220.365)
	261.420	Fe* (261.187 and 261.382), Ca*#, Co* (261.534), Mg*#, Mn**
	405.780	Mn (405.795), V (405.783), Zn (405.771)
	257.610	Mg (257.606)
	259.372	Fe (259.373), Mo (259.371)
mercury	260.568	Co (260.574), Fe (260.562)
	294.920	V (294.919), Fe (294.915)
	184.887	Si (184.812, 184.752), As (184.962)
molybdenum	194.164	V (194.174, 194.076), Co (194.064)
	202.032	Fe (202.075), Ni (202.098)
nickel	204.598	Cr (204.533)
	221.648	Mo (221.666), Ti (221.666), Co (221.638), Cr (221.635)
	231.604	Co (231.616), Sb (231.588)
	232.003	Cr* (232.009), Mo (232.008), Co (231.987), V (232.016)
selenium	341.476	Co* (341.474), V (341.488)
	196.026	Fe (195.950, 196.061), Bi (195.941)
thallium	203.986	Cr (203.991), Sb (203.977), Mn (203.998)
	276.787	Fe (276.752 and 276.811)
vanadium	292.402	Fe (292.388), Cr (292.372)
	309.310	Mg* (309.299), Al* (309.271)
	310.230	Ni (310.193)
zinc	311.071	Mn (311.068), Fe (311.071), Mg (311.053), Cr (311.086)
	202.548	Cu* (202.548), Cr (202.563), Ni (202.538), Fe (202.544)
	206.200	Mo (206.198), Mg (206.196), Fe (206.207)
	213.857	Ni (213.858), Cu (213.851), Ca (213.865), Fe (213.859), Mg (213.856)
	334.501	Mo* (334.475), Ca* (334.444), Ti#

Taken in part from references 4 and 16 - 19.

In addition to these major interferences, the 361.051 nm wavelength suffers more interferences and exhibits a poor peak shape. * Major interferent at that wavelength.

Baseline caused by an interferent that has greater intensity than the analyte signal.

Table 2 Possible interferences for selected metals with ICP-MS

Isotope	Relative abundance (%)	Possible interferences
9 beryllium	100	$^{18}\text{O}^{2+}$
50 chromium	4.3	$^{40}\text{Ar-}^{10}\text{B}^+$, $^{100}\text{Ru}^{2+}$, $^{100}\text{Mo}^{2+}$, $^{50}\text{Ti}^+$, $^{34}\text{S-}^{16}\text{O}^+$, $^{36}\text{Ar-}^{14}\text{N}^+$, $^{50}\text{V}^+$, $^{38}\text{Ar-}^{12}\text{C}^+$
50 vanadium	0.3	$^{40}\text{Ar-}^{10}\text{B}^+$, $^{100}\text{Ru}^{2+}$, $^{100}\text{Mo}^{2+}$, $^{50}\text{Ti}^+$, $^{50}\text{Cr}^+$, $^{34}\text{S-}^{16}\text{O}^+$, $^{36}\text{Ar-}^{14}\text{N}^+$, $^{38}\text{Ar-}^{12}\text{C}^+$
51 vanadium	99.8	$^{40}\text{Ar-}^{11}\text{B}^+$, $^{36}\text{Ar-}^{15}\text{N}^+$, $^{36}\text{Ar-}^{14}\text{N-}^1\text{H}^+$, $^{35}\text{Cl-}^{16}\text{O}^+$, $^{102}\text{Ru}^{2+}$, $^{37}\text{Cl-}^{14}\text{N}^+$, $^{34}\text{S-}^{16}\text{O-}^1\text{H}^+$
52 chromium	83.8	$^{38}\text{Ar-}^{14}\text{N}^+$, $^{36}\text{Ar-}^{15}\text{N-}^1\text{H}^+$, $^{40}\text{Ar-}^{12}\text{C}^+$, $^{35}\text{Cl-}^{16}\text{O-}^1\text{H}^+$, $^{104}\text{Ru}^{2+}$, $^{104}\text{Pd}^{2+}$, $^{36}\text{Ar-}^{16}\text{O}^+$
53 chromium	9.5	$^{106}\text{Pd}^{2+}$, $^{37}\text{Cl-}^{16}\text{O}^+$, $^{106}\text{Cd}^{2+}$, $^{40}\text{Ar-}^{13}\text{C}^+$, $^{38}\text{Ar-}^{15}\text{N}^+$, $^{35}\text{Cl-}^{18}\text{O}^+$
54 chromium	2.4	$^{40}\text{Ar-}^{14}\text{N}^+$, $^{108}\text{Pd}^{2+}$, $^{37}\text{Cl-}^{16}\text{O-}^1\text{H}^+$, $^{54}\text{Fe}^+$, $^{108}\text{Cd}^{2+}$
54 iron	5.8	$^{54}\text{Cr}^+$, $^{38}\text{Ar-}^{16}\text{O}^+$
55 manganese	100	$^{40}\text{Ar-}^{14}\text{N-}^1\text{H}^+$, $^{39}\text{K-}^{16}\text{O}^+$, $^{110}\text{Pd}^{2+}$, $^{110}\text{Cd}^{2+}$, $^{40}\text{Ar-}^{15}\text{N}^+$
56 iron	91.7	$^{40}\text{Ca-}^{16}\text{O}^+$, $^{40}\text{Ar-}^{16}\text{O}^+$
57 iron	2.2	$^{41}\text{K-}^{16}\text{O}^+$, $^{39}\text{K-}^{18}\text{O}^+$
58 iron	0.3	$^{23}\text{Na-}^{35}\text{Cl}^+$, $^{116}\text{Sn}^{2+}$, $^{116}\text{Cd}^{2+}$, $^{42}\text{Ca-}^{16}\text{O}^+$, $^{58}\text{Ni}^+$, $^{40}\text{Ar-}^{18}\text{O}^+$
58 nickel	68.1	$^{23}\text{Na-}^{35}\text{Cl}^+$, $^{116}\text{Sn}^{2+}$, $^{116}\text{Cd}^{2+}$, $^{42}\text{Ca-}^{16}\text{O}^+$, $^{58}\text{Fe}^+$, $^{40}\text{Ar-}^{18}\text{O}^+$
59 cobalt	100	$^{40}\text{Ar-}^{19}\text{F}^+$, $^{118}\text{Sn}^{2+}$, $^{36}\text{Ar-}^{23}\text{Na}^+$, $^{40}\text{Ar-}^{18}\text{O-}^1\text{H}^+$
60 nickel	26.2	$^{120}\text{Sn}^{2+}$, $^{23}\text{Na-}^{37}\text{Cl}^+$, $^{44}\text{Ca-}^{16}\text{O}^+$
61 nickel	1.1	$^{45}\text{Sc-}^{16}\text{O}^+$, $^{122}\text{Sn}^{2+}$, $^{122}\text{Te}^{2+}$, $^{38}\text{Ar-}^{23}\text{Na}^+$, $^{36}\text{Ar-}^{25}\text{Mg}^+$
62 nickel	3.6	$^{46}\text{Ti-}^{16}\text{O}^+$, $^{124}\text{Sn}^{2+}$, $^{124}\text{Te}^{2+}$, $^{36}\text{Ar-}^{26}\text{Mg}^+$
63 copper	69.2	$^{40}\text{Ar-}^{23}\text{Na}^+$, $^{31}\text{P-}^{16}\text{O}_2^+$, $^{126}\text{Te}^{2+}$, $^{46}\text{Ti-}^{16}\text{O-}^1\text{H}^+$, $^{47}\text{Ti-}^{16}\text{O}^+$
64 nickel	0.9	$^{32}\text{P-}^{16}\text{O}_2^+$, $^{32}\text{S-}^{16}\text{O}_2^+$, $^{32}\text{S}_2^+$, $^{40}\text{Ar-}^{24}\text{Mg}^+$, $^{48}\text{Ti-}^{16}\text{O}^+$, $^{64}\text{Zn}^+$, $^{128}\text{Te}^{2+}$, $^{47}\text{Ti-}^{16}\text{O-}^1\text{H}^+$, $^{64}\text{Ni}^+$
64 zinc	48.6	$^{32}\text{S-}^{16}\text{O}_2^+$, $^{32}\text{S-}^{32}\text{S}^+$, $^{40}\text{Ar-}^{24}\text{Mg}^+$, $^{48}\text{Ti-}^{16}\text{O}^+$, $^{128}\text{Te}^{2+}$, $^{47}\text{Ti-}^{16}\text{O-}^1\text{H}^+$, $^{64}\text{Ni}^+$
65 copper	30.8	$^{48}\text{Ti-}^{16}\text{O-}^1\text{H}^+$, $^{130}\text{Te}^{2+}$, $^{40}\text{Ar-}^{25}\text{Mg}^+$, $^{49}\text{Ti-}^{16}\text{O}^+$, $^{32}\text{S-}^{33}\text{S}^+$, $^{33}\text{S-}^{16}\text{O-}^{16}\text{O}^+$, $^{130}\text{Ba}^{2+}$
66 zinc	27.9	$^{40}\text{Ar-}^{26}\text{Mg}^+$, $^{32}\text{S-}^{34}\text{S}^+$, $^{49}\text{Ti-}^{16}\text{O-}^1\text{H}^+$, $^{50}\text{Ti-}^{16}\text{O}^+$, $^{50}\text{Cr-}^{16}\text{O}^+$, $^{34}\text{S-}^{16}\text{O}_2^+$, $^{132}\text{Ba}^{2+}$
67 zinc	4.1	$^{40}\text{Ar-}^{27}\text{Al}^+$, $^{40}\text{Ar-}^{14}\text{N}_2^+$, $^{51}\text{V-}^{16}\text{O}^+$, $^{35}\text{Cl-}^{16}\text{O}_2^+$, $^{50}\text{Ti-}^{16}\text{O-}^1\text{H}^+$, $^{134}\text{Ba}^{2+}$, $^{36}\text{Ar-}^{31}\text{P}^+$
68 zinc	18.8	$^{40}\text{Ar-}^{28}\text{Si}^+$, $^{52}\text{Cr-}^{16}\text{O}^+$, $^{136}\text{Ba}^{2+}$, $^{136}\text{Ce}^{2+}$
70 zinc	0.6	$^{140}\text{Ce}^{2+}$, $^{35}\text{Cl-}^{35}\text{Cl}^+$, $^{70}\text{Ge}^+$, $^{54}\text{Fe-}^{16}\text{O}^+$, $^{40}\text{Ar-}^{30}\text{Si}^+$, $^{54}\text{Cr-}^{16}\text{O}^+$, $^{40}\text{Ar-}^{14}\text{N-}^{16}\text{O}^+$
75 arsenic	100	$^{40}\text{Ar-}^{35}\text{Cl}^+$, $^{150}\text{Nd}^{2+}$, $^{150}\text{Sm}^{2+}$
76 selenium	9.4	$^{76}\text{Ge}^+$, $^{152}\text{Gd}^{2+}$
77 selenium	7.6	$^{40}\text{Ar-}^{37}\text{Cl}^+$, $^{154}\text{Sm}^{2+}$, $^{154}\text{Gd}^{2+}$
78 selenium	23.8	$^{78}\text{Kr}^+$
80 selenium	49.6	$^{80}\text{Kr}^+$
82 selenium	8.7	$^{82}\text{Kr}^+$, $^{40}\text{Ar-}^{42}\text{Ca}^+$, $^{164}\text{Dy}^{2+}$, $^{164}\text{Er}^{2+}$, $^{81}\text{Br-}^1\text{H}^+$
95 molybdenum	15.9	$^{79}\text{Br-}^{16}\text{O}^+$
96 molybdenum	16.7	$^{96}\text{Zr}^+$, $^{96}\text{Ru}^+$
98 molybdenum	24.1	$^{98}\text{Ru}^+$
100 molybdenum	9.6	$^{100}\text{Ru}^+$
106 cadmium	1.3	$^{90}\text{Zr-}^{16}\text{O}^+$, $^{40}\text{Ar-}^{66}\text{Zn}^+$, $^{106}\text{Pd}^+$, $^{88}\text{Sr-}^{18}\text{O}^+$
108 cadmium	0.9	$^{108}\text{Pd}^+$, $^{40}\text{Ar-}^{68}\text{Zn}^+$, $^{92}\text{Zr-}^{16}\text{O}^+$, $^{92}\text{Mo-}^{16}\text{O}^+$
110 cadmium	12.5	$^{40}\text{Ar-}^{70}\text{Ge}^+$, $^{94}\text{Zr-}^{16}\text{O}^+$, $^{110}\text{Pd}^+$, $^{94}\text{Mo-}^{16}\text{O}^+$, $^{40}\text{Ar-}^{70}\text{Zn}^+$
111 cadmium	12.8	$^{79}\text{Br-}^{32}\text{S}^+$, $^{40}\text{Ar-}^{71}\text{Ga}^+$, $^{95}\text{Mo-}^{16}\text{O}^+$, $^{36}\text{Ar-}^{75}\text{As}^+$
112 cadmium	24.1	$^{40}\text{Ar-}^{72}\text{Ge}^+$, $^{96}\text{Mo-}^{16}\text{O}^+$, $^{96}\text{Ru-}^{16}\text{O}^+$, $^{96}\text{Zr-}^{16}\text{O}^+$, $^{112}\text{Sn}^+$, $^{79}\text{Br-}^{33}\text{S}^+$
113 cadmium	12.2	$^{81}\text{Br-}^{32}\text{S}^+$, $^{97}\text{Mo-}^{16}\text{O}^+$, $^{40}\text{Ar-}^{73}\text{Ge}^+$, $^{113}\text{In}^+$, $^{38}\text{Ar-}^{75}\text{As}^+$
114 cadmium	28.7	$^{79}\text{Br-}^{35}\text{Cl}^+$, $^{40}\text{Ar-}^{74}\text{Ge}^+$, $^{98}\text{Mo-}^{16}\text{O}^+$, $^{98}\text{Ru-}^{16}\text{O}^+$, $^{40}\text{Ar-}^{74}\text{Se}^+$, $^{114}\text{Sn}^+$
116 cadmium	7.5	$^{232}\text{Th}^{2+}$, $^{81}\text{Br-}^{35}\text{Cl}^+$, $^{116}\text{Sn}^+$, $^{100}\text{Ru-}^{16}\text{O}^+$, $^{100}\text{Mo-}^{16}\text{O}^+$, $^{40}\text{Ar-}^{76}\text{Se}^+$, $^{40}\text{Ar-}^{76}\text{Ge}^+$
121 antimony	57.4	$^{105}\text{Pd-}^{16}\text{O}^+$, $^{103}\text{Rh-}^{16}\text{O}^+$
123 antimony	42.6	$^{123}\text{Te}^+$, $^{107}\text{Ag-}^{16}\text{O}^+$, $^{105}\text{Pd-}^{18}\text{O}^+$
135 barium	6.6	$^{119}\text{Sn-}^{16}\text{O}^+$
136 barium	7.9	$^{136}\text{Ce}^+$, $^{136}\text{Xe}^+$, $^{120}\text{Sn-}^{16}\text{O}^+$
137 barium	11.2	$^{121}\text{Sb-}^{16}\text{O}^+$
138 barium	71.7	$^{138}\text{Ce}^+$, $^{138}\text{La}^+$
198 mercury	10	$^{198}\text{Pt}^+$, $^{182}\text{W-}^{16}\text{O}^+$
199 mercury	16.9	$^{183}\text{W-}^{16}\text{O}^+$
200 mercury	23.1	$^{184}\text{W-}^{16}\text{O}^+$
201 mercury	13.2	$^{185}\text{Re-}^{16}\text{O}^+$
202 mercury	29.9	$^{186}\text{W-}^{16}\text{O}^+$, $^{186}\text{Os-}^{16}\text{O}^+$
204 mercury	6.9	$^{204}\text{Pb}^+$, $^{188}\text{Os-}^{16}\text{O}^+$
203 thallium	29.5	$^{187}\text{Re-}^{16}\text{O}^+$, $^{187}\text{Os-}^{16}\text{O}^+$
205 thallium	70.5	$^{189}\text{Os-}^{16}\text{O}^+$
204 lead#	1.4	$^{188}\text{Os-}^{16}\text{O}^+$, $^{204}\text{Hg}^+$
206 lead#	24.1	$^{190}\text{Os-}^{16}\text{O}^+$
207 lead#	22.1	$^{191}\text{Ir-}^{16}\text{O}^+$
208 lead#	52.4	$^{192}\text{Os-}^{16}\text{O}^+$

Taken in part from references 4 and 16 - 19.

These ratios may change depending on the geological area in which the lead originates.

6 References

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- 18 ISO / DIS 11885:2004 - Water Quality - Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES).
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A The determination of selected elements in soils by *aqua regia* extraction using inductively coupled plasma-mass spectrometry

A1 Performance characteristics of method

A1.1	Substances determined	Aluminium, arsenic, antimony, barium, beryllium, cadmium, calcium, cobalt, copper, chromium, gallium, indium, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, phosphorus, potassium, selenium, silver, sodium, strontium, thallium, tin, titanium, vanadium and zinc.
A1.2	Type of sample	Contaminated land and soils.
A1.3	Basis of the method	Metals contained within the soil or contaminated land are extracted with <i>aqua regia</i> . The resulting solution is filtered and the filtrate diluted with nitric acid. Quantification is determined using inductively coupled plasma-mass spectrometry.
A1.4	Range of application	Up to 20 mg/kg for mercury. Up to 50 mg/kg for antimony, beryllium and selenium. Up to 200 mg/kg for arsenic, cadmium, cobalt, gallium, indium, molybdenum, silver, tin, thallium and vanadium. Up to 2000 mg/kg for barium, copper, chromium, lead, manganese, nickel, strontium, titanium and zinc. Up to 20000 mg/kg for aluminium, calcium, iron, magnesium, phosphorus, potassium and sodium.
A1.5	Performance data	See Table A1.
A1.6	Interferences	Oxides, doubly charged ions and high levels of chloride. Interferences (caused by the presence of chloride) are reduced by diluting the extract solution with dilute nitric acid.

A2 Principle

The sample of soil or contaminated land is extracted with boiling *aqua regia*. The extract is cooled and filtered, and the resulting solution diluted with nitric acid. Inductively coupled plasma-mass spectrometry is used for quantification and the resulting ion emission spectra quantified using a quadrupole mass spectrometer. Metal concentrations are determined against calibration standard solutions similarly diluted.

A3 Hazards

Appropriate personal protective equipment should be worn when handling reagents and potentially contaminated samples. Concentrated acids should always be added to water and operations carried out in a fume cupboard. The extract solutions contain concentrated acids and should be handled with care.

A4 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interference in the analysis. This should be checked for each batch of chemicals and reagents and verified by running reagent blanks with each batch of samples analysed. Reagents should be stored in tightly sealed containers or other suitable vessels and stored at room temperature and kept in the dark, if necessary.

Water should be deionised (specific conductivity of less than 10 $\mu\text{S}/\text{cm}$) and volumetric glassware should be of at least grade B quality. All reagents should be appropriately labelled, including the expiry date of the reagent. The preparation of all reagents should be recorded.

A4.1 Concentrated nitric acid (SG 1.42).

A4.2 Concentrated hydrochloric acid (SG 1.18).

A4.3 Internal standard stock solution (5 mg/l of Sc, Ge, Rh and Ir). To a 1000-ml volumetric flask, add approximately 500 ml of water. To the flask, add 5.0 ml of 1000 mg/l scandium standard solution and 5.0 ml of 1000 mg/l germanium standard solution. Also, add 5.0 ml of 1000 mg/l rhodium standard solution and 5.0 ml of 1000 mg/l iridium standard solution. Add 50 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 990 ml and allow the solution to cool. Mix thoroughly. Make to 1000 ml with water and mix. This reagent may be stored at room temperature and kept for up to three months. These metals should not be present in the soil at significant levels.

A4.4 Internal standard/diluent solution (100 $\mu\text{g}/\text{l}$ of Sc, Ge, Rh and Ir, and 200 $\mu\text{g}/\text{l}$ of Au). To a 1000-ml volumetric flask, add approximately 500 ml of water. To the flask, add 20.0 ml of internal standard stock solution (A4.3) and 20.0 ml of 10 mg/l gold standard solution (A4.6). Add 50 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 990 ml and allow the solution to cool. Mix thoroughly. Make to 1000 ml with water and mix. This reagent should be prepared on the day of use. Gold is added to this solution to prevent mercury adhering to the internal surfaces of the instrument sample introduction system, for example tubing, spray chamber and nebuliser. Ensure there is sufficient of this internal standard and diluent solution to complete the analysis.

A4.5 Gold solution (100 mg/l). To a 100-ml volumetric flask, add approximately 50 ml of water. To the flask, add 1.0 ml of 10000 mg/l gold standard solution. Add 5.0 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 99 ml and allow the solution to cool. Mix thoroughly. Make to 100 ml with water and mix. This reagent may be stored at room temperature and kept for up to six months.

A4.6 Gold solution (10 mg/l). To a 1000-ml volumetric flask, add approximately 500 ml of water. To the flask, add 1.0 ml of 10000 mg/l gold standard solution. Add 50 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 990 ml

and allow the solution to cool. Mix thoroughly. Make to 1000 ml with water and mix. This reagent may be stored at room temperature and kept for up to three months.

A4.7 Rinse solution. To a 1000-ml volumetric flask, add approximately 500 ml of water. To the flask, add 50 ml concentrated nitric acid (A4.1). Dilute the solution with water to approximately 970 ml and allow the solution to cool. Add 20.0 ml of 10 mg/l gold solution (A4.6). Mix thoroughly. Make to 1000 ml with water and mix. This reagent should be prepared on the day of use. Gold is added to this solution to prevent mercury adhering to the internal surfaces of the instrument sample introduction system, for example tubing, spray chamber and nebuliser. This solution is used to rinse the auto-sampler probe between sample determinations.

A4.8 Tuning intermediate solution (10 mg/l of Co). To a 100-ml volumetric flask, add approximately 50 ml of water. To the flask, add 1.0 ml of 1000 mg/l cobalt standard solution. Dilute the solution with water to approximately 99 ml and mix thoroughly. Make to 100 ml with water and mix. This reagent may be stored at room temperature and kept for up to three months.

A4.9 Tuning solution (10 µg/l of Li, Y, Ce, Tl and Co). To a 1000-ml volumetric flask, add approximately 500 ml of water. To the flask, add 1.0 ml of tuning intermediate solution (A4.8) and 1.0 ml of a stock solution containing 10 mg/l of each element, lithium, yttrium, cerium and thallium. Add 20 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 990 ml and allow the solution to cool. Mix thoroughly. Make to 1000 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.10 Standard preparation. All standard solutions should be stored in plastic bottles and kept at room temperature. Stock standard solutions are commercially available.

A4.10.1 Intermediate calibration solution A (40 mg/l of Mo, Sn and V). To a 100-ml volumetric flask, add approximately 50 ml of water. To the flask, add 4.0 ml of 1000 mg/l molybdenum standard solution, 4.0 ml of 1000 mg/l tin standard solution and 4.0 ml of 1000 mg/l vanadium standard solution. Add 5.0 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 99 ml and mix thoroughly. Make to 100 ml with water and mix. This reagent may be stored at room temperature and kept for up to three months.

A4.10.2 Intermediate calibration solution B (20 mg/l of Hg). To a 100-ml volumetric flask, add approximately 50 ml of water. To the flask, add 2.0 ml of 1000 mg/l mercury standard solution, 5.0 ml of gold solution (A4.5) and 5.0 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 99 ml and mix thoroughly. Make to 100 ml with water and mix. This reagent may be stored at room temperature and kept for up to three months.

A4.10.3 Intermediate calibration solution C (200 mg/l of As, and 50 mg/l of Se, Sb and Be). To a 100-ml volumetric flask, add approximately 50 ml of water. To the flask, add 20.0 ml of 1000 mg/l arsenic standard solution. Add 5.0 ml of 1000 mg/l selenium standard solution, 5.0 ml of 1000 mg/l antimony standard solution and 5.0 ml of 1000 mg/l beryllium standard solution. Add 5.0 ml of concentrated nitric acid (A4.1) and dilute the solution with water to approximately 99 ml. Mix thoroughly. Make to 100 ml with water and mix. This reagent may be stored at room temperature and kept for up to three months.

A4.11 Working calibration standard solutions.

A4.11.1 Blank calibration standard solution 1. To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 105 ml of concentrated hydrochloric acid (A4.2) and 35 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.2 Calibration standard solution 2 (200 µg/l of Ag, Ba, Cd, Co, Cr, Cu, Ga, In, Mn, Ni, Pb, Sr, Tl, Zn, Sn, V, Mo and Ti). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 50.0 ml of calibration standard solution 4 (A4.11.4) and 94.5 ml of concentrated hydrochloric acid (A4.2) and 31.5 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.3 Calibration standard solution 3 (1000 µg/l of Ag, Ba, Cd, Co, Cr, Cu, Ga, In, Mn, Ni, Pb, Sr, Tl, Zn, Sn, V, Mo and Ti). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 25.0 ml of calibration standard solution 6 (A4.11.6) and 12.5 ml of intermediate calibration solution A (A4.10.1) and 100 ml of concentrated hydrochloric acid (A4.2) and 33 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.4 Calibration standard solution 4 (2000 µg/l of Ag, Ba, Cd, Co, Cr, Cu, Ga, In, Mn, Ni, Pb, Sr, Tl, Zn, Sn, V, Mo and Ti). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 50.0 ml of calibration standard solution 6 (A4.11.6) and 25.0 ml of intermediate calibration solution A (A4.10.1) and 94.5 ml of concentrated hydrochloric acid (A4.2) and 31.5 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.5 Calibration standard solution 5 (10000 µg/l of Ba, Cr, Cu, Mn, Ni, Pb, Sr, Zn and Ti). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 5.0 ml of a multi-element standard solution containing 1000 mg/l of each of the following elements, barium, chromium, copper, lead, manganese, nickel, strontium and zinc. Add 5.0 ml of 1000 mg/l titanium standard solution and 105 ml of concentrated hydrochloric acid (A4.2) and 35 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.6 Calibration standard solution 6 (20000 µg/l of Ba, Cr, Cu, Mn, Ni, Pb, Sr, Zn and Ti). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 10.0 ml of a multi-standard solution containing 1000 mg/l of each of the following elements, barium, chromium, copper, lead, manganese, nickel, strontium and zinc. Add 10.0 ml of 1000 mg/l titanium standard solution and 105 ml of concentrated hydrochloric acid (A4.2) and 35 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with

water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.7 Calibration standard solution 7 (20 µg/l of Hg). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 50.0 ml of calibration standard solution 9 (A4.11.9) and 94.5 ml of concentrated hydrochloric acid (A4.2) and 31.5 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.8 Calibration standard solution 8 (100 µg/l of Hg). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 2.5 ml of intermediate calibration solution B (A4.10.2) and 105 ml of concentrated hydrochloric acid (A4.2) and 35 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.9 Calibration standard solution 9 (200 µg/l of Hg). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 5.0 ml of intermediate calibration solution B (A4.10.2) and 105 ml of concentrated hydrochloric acid (A4.2) and 35 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.10 Calibration standard solution 10 (20 mg/l of Na, K, Ca, Mg, Fe, P and Al). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 50.0 ml of calibration standard solution 12 (A4.11.12) and 94.5 ml of concentrated hydrochloric acid (A4.2) and 31.5 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.11 Calibration standard 11 (100 mg/l of Na, K, Ca, Mg, Fe, P and Al). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 5.0 ml of 10000 mg/l sodium standard solution, 5.0 ml of 10000 mg/l potassium standard solution, 5.0 ml of 10000 mg/l calcium standard solution and 5 ml of 10000 mg/l magnesium standard solution. Add 5.0 ml of 10000 mg/l iron standard solution, 5.0 ml of 10000 mg/l phosphorus standard solution and 5.0 ml of 10000 mg/l aluminium standard solution. Add 105 ml of concentrated hydrochloric acid (A4.2) and 35 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.12 Calibration standard 12 (200 mg/l of Na, K, Ca, Mg, Fe, P and Al). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 10.0 ml of 10000 mg/l sodium standard solution and 10.0 ml of 10000 mg/l potassium standard solution. Add 10.0 ml of 10000 mg/l calcium standard solution and 10.0 ml of 10000 mg/l magnesium standard solution. Add 10.0 ml of 10000 mg/l iron standard solution, 10.0 ml of 10000 mg/l phosphorus standard solution and 10.0 ml of 10000 mg/l aluminium standard solution. Add 105 ml of concentrated hydrochloric acid (A4.2) and 35 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the

solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.13 Calibration standard solution 13 (200 µg/l of As and 50 µg/l of Se, Sb and Be). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 50.0 ml of calibration standard solution 14 (A4.11.14) and 94.5 ml of concentrated hydrochloric acid (A4.2) and 31.5 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.14 Calibration standard 14 (1000 µg/l As, and 250 µg/l Se, Sb and Be). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 2.5 ml of intermediate calibration solution C (A4.10.3) and 105 ml of concentrated hydrochloric acid (A4.2) and 35 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A4.11.15 Calibration standard solution 15 (2000 µg/l of As and 500 µg/l of Se, Sb and Be). To a 500-ml volumetric flask, add approximately 250 ml of water. To the flask, add 5.0 ml of intermediate calibration solution C (A4.10.3) and 105 ml of concentrated hydrochloric acid (A4.2) and 35 ml of concentrated nitric acid (A4.1). Dilute the solution with water to approximately 490 ml and allow the solution to cool. Mix thoroughly. Make to 500 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

A5 Apparatus

Glassware should be washed using a detergent solution, for example Decon-90 or equivalent and rinsed with water. The glassware should then be soaked in acid solution, for example, 10 % nitric acid, for a minimum of one hour. Glassware should then be rinsed with water, drained, and allowed to dry.

A5.1 Volumetric flasks: 100 ml, 500 ml, 100 ml.

A5.2 Auto-pipettes (variable): 0.1-1 ml, 1-5 ml, 1-10 ml.

A5.3 Inductively coupled plasma mass spectrometer with octapole reaction/collision cell and babbington nebuliser.

A5.4 Auto-sampler vials: 15 ml.

A5.5 Top pan balance capable of weighing to ± 0.01 g.

A5.6 Conical flasks: 100 ml.

A5.7 Air condensers.

A5.8 Dispensers: 2 – 10 ml.

A5.9 Filter funnels.

A5.10 Hardened filter papers (capable of fast flow rates): For example Whatman 541 filter papers, or equivalent.

A5.11 Hot-plate.

A5.12 Pump tubing.

A5.13 Gases: Argon, > 99.99 %; Hydrogen, ≥ 99.999 %; Helium, ≥ 99.999 %.

A6 Sample preparation

This method has been performance tested using air-dried samples (i.e. air at less than 30 °C passed over the soil) and may not be suitable for samples containing significant amounts of water. The use of an air-dried sample rather than an “as received” sample enables a more homogeneous sub-sample to be taken for analysis. The procedures used to prepare crushed, ground, sieved and/or air-dried samples may, however, adversely affect some metals and metal species present in the original sample prior to analysis. This is particularly the case for mercury, which may be lost in the drying process used to prepare the air-dried sample, even at ambient temperatures. Analysts should, therefore, ascertain whether the procedures used to prepare crushed, ground, sieved and/or air-dried samples affect the resulting determination of metal concentrations. In addition, great care should be taken to ensure that the sub-sample is homogeneous, and representative of the bulk material sampled, especially when smaller quantities are required for repeat analyses where high concentrations are found or suspected.

A7 Analytical procedure

Step	Procedure	Note
A7.1	Weigh out 1.0 g of the prepared soil or contaminated land sample (A6) into a 100-ml glass conical flask. See note a. To the flask and ensuring that the neck of the flask is clean, add 7.0 ml of concentrated nitric acid (A4.1). Fit an air condenser to the flask. Add 21.0 ml of concentrated hydrochloric acid (A4.2) to the flask via the condenser and swirl to mix.	(a) If samples are to be reported on a dry weight basis (at 105 °C) rather than on an air-dried basis, (for example at 30 °C or 40 °C) it will be necessary to carry out a dry solids content determination on a separate portion of the air-dried material. The result should be expressed as percent dried solids.
A7.2	Allow the flask to stand at room temperature for at least 20 minutes until any reaction subsides, see note b. Place the flask on a pre-heated hot-plate at a temperature sufficient to reflux the <i>aqua regia</i> . Observe the contents of the flask for several minutes to ensure that any initial reaction is not too vigorous, see note c.	(b) If a vigorous reaction occurs, add a small amount of water slowly down the air condenser until the reaction subsides. Continue to monitor the reaction and repeat if necessary. (c) If the reaction is vigorous, remove the flask from the hot-plate, add a small amount of water slowly down the air condenser until the reaction subsides and return the flask to the hot-plate. Continue to monitor the

reaction and repeat if necessary.

A7.3 Gently reflux the contents of the flask for 180 minutes, then remove the flask from the hot-plate and allow to cool to room temperature. Rinse down the air condenser with 20 ml of water and remove the condenser.

A7.4 Filter the cooled extract solution through a filter paper (A5.10) into a 100-ml volumetric flask. Rinse the conical flask with water and filter the rinsings through the filter paper into the volumetric flask. Make to volume with water.

A7.5 Prepare reagent blanks as required using the procedures described in sections A7.1 - A7.4 using the same batch of reagents used for the samples.

A7.6 Prepare an AQC spiked soil sample using an appropriate soil matrix. Commercially available dried and ground soils may be available. See note d.

A7.7 Following manufacturer's instructions, use the tuning solution (A4.9) to tune the mass spectrometer. The isotopic mass numbers used for monitoring purposes are shown in Table A2. Adjust the instrument to maximise the counts, and reduce the formation of doubly charged ions and interfering ions of oxides. See note e.

A7.8 Using the isotopic mass numbers shown in Table A2, analyse the calibration standard solutions (A4.11.1 - A4.11.15) blank solutions, sample extract solutions and any AQC solutions. See notes e and f. Between each determination the rinse solution (A4.7) should be used to rinse the auto-sampler.

(d) For example, spike 1 g of soil with an appropriate amount of metal and extract the soil following procedures described in sections A7.1 - A7.4.

(e) Solutions are diluted online (for example by a factor of twenty) with internal standard/diluent solution (A4.4) prior to measurement (in order to minimise chloride interference and correct for instrument drift effects). As the calibration standard solutions, blank solutions, AQC solutions and sample extract solutions are all treated in the same manner there is no need to correct for this dilution.

(f) For any sample extract solution giving a result outside of the calibration range, the extract (A7.4) should be diluted accordingly or consideration given to repeating the analysis using a smaller quantity of sample (A7.1) or using more *aqua regia* and making to a larger volume (A7.4).

A8 Calculations

The concentration of the element in the sample is given by:

$$C_{\text{sample}} = (C_{\text{extract}} \times V_{\text{extract}} \times \text{DF}) / M_{\text{sample}}$$

Where C_{sample} is the concentration of the element in the air-dried sample (mg/kg);
 C_{extract} is the concentration of element in the sample extract solution (mg/l);
 V_{extract} is the volume of extract (ml, usually 100 ml, section A7.4);
DF is the dilution factor, if any (note f, section A7.8); and
 M_{sample} is the mass of sample (g, usually 1 g, section A7.1).

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed. In addition, the reporting of results may also need to take into account whether results are calculated on an air-dried basis (for example at 30 °C) or on a dry weight basis (at 105 °C).

When an air-dried sample is prepared, and from this say A % of inert extraneous material is removed, then if (excluding inert extraneous material)

$$\text{moisture content on air-dried matter} = B \%$$

and

$$\text{metal concentration on air-dried matter} = C \text{ mg/kg}$$

then

$$\text{metal concentration on dry weight basis} = (C \times 100) / (100 - B) \text{ mg/kg}$$

If the inert extraneous material needs to be taken into account, then

$$\text{metal concentration on air-dried matter} = (C \times (100-A))/100 \text{ mg/kg}$$

and

$$\text{metal concentration on dry weight basis} = ((C \times 100) / (100 - B)) \times ((100 - ((A \times 100) / (100 - B))) / 100) \text{ mg/kg}$$

Table A1 Performance data

Element	LOD (mg/kg)	7002 Sand			Certified Reference Material 7003 Clay			7004 Loam		
		CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)
arsenic	0.4	26.1	3.1	3.7	11.6	6.6	8.6	42.4	3.3	8.6
barium	2	99.1	4.7	4.3	146	11.1	3.1	217	6.3	3.4
chromium	2	147	4.2	2.6	42.4	9.3	4.1	46.3	8.9	3.6
cobalt	0.2	11.1	3.8	-3.7	10.3	6.5	-4.1	17.5	4.3	-2.7
copper	2	27.3	4.1	0.2	25.4	5.2	0.3	167	3.2	5.2
lead	2	35.5	3.4	7.8	25.2	5.2	5.4	83.1	3.0	5.1
manganese	2	531	3	1.4	529	4.3	0.9	741	4.6	-1
mercury	0.1	0.08*	77.7	25	0.093*	420	-46	0.21	56	31
nickel	2	40.1	1.9	5.0	28.8	2.7	2.9	30.4	3.2	3.2
vanadium	2	44.6	3.9	-4.5	52.9	6.6	-5.1	95.1	6.2	-10.9
zinc	3	64	4.7	3.8	69.4	4.8	1.2	198	3.1	5.4

* below method LOD

Element	LOD (mg/kg)	Certified Reference Material NIST 2711			ERA 540		
		CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)
aluminium	23				7270	10.8	31
antimony	0.2	19.4	4.4	-12.1			
beryllium	0.1				62.5	4.2	2.5
cadmium	0.2	41.7	2.9	-5.7	110	4.4	4.0
calcium	51				4120	8.9	1.9
gallium	0.7	15	7.7	-23.4			
indium	0.3	1.1	34.2	-12.5			
iron	33	28900	8.7	-19.6			
magnesium	9				2380	7.1	15.2
mercury	0.1				8.38	6.1	11.5
molybdenum	0.3				62.9	2.3	11.5
phosphorus	29	860	4.9	-17.6			
potassium	246				1880	31	19.1
selenium	0.2				94.4	6.2	-0.1
silver	0.8				102	2.4	6.7
sodium	60				871	7.9	4.2
strontium	0.4				117	3.8	7.9
thallium	0.9				88.6	3.9	1.3
tin	0.3				89.5	3.6	7.2
titanium	1				322	8.9	161

Performance data provided by Analytical and Environmental Services Ltd.

LOD is calculated as 5 x within batch standard deviation of blank soil extracts (acid washed quartz), following analysis of 11 batches in duplicate.

CRM 7002 is a dried homogenised sieved sand soil to less than 100 µm.

CRM 7003 is a dried homogenised sieved clay soil to less than 100 µm.

CRM 7004 is a dried homogenised sieved loam soil to less than 100 µm.

CRM NIST 2711 is a dried homogenised sieved moderately contaminated agricultural soil to less than 74 µm.

CRM ERA 540 is a dried homogenised inorganic soil.

Results with a high bias may indicate that the CRM value may need to be checked (for example total or extractable value and methodology used to generate the reference value) or that the procedure used for that element may be inappropriate for the determination of that element in the matrix.

Table A2 Elements and mass numbers monitored

Element	Mass	Internal standard
lithium*	7	45 (scandium)
beryllium	9	45
sodium	23	45
magnesium	24	45
aluminium	27	45
phosphorus	31	45
potassium	39	45
calcium	44	45
titanium	47	45
vanadium	51	45
chromium	52	72(germanium)
manganese	55	45
iron	56	45
cobalt*	59	72
nickel	60	72
copper	63	74(germanium)
zinc	66	72
gallium	69	72
arsenic	75	74
selenium	78	74
strontium	88	103(rhodium)
yttrium*	89	
molybdenum	95	103
silver	107	103
cadmium	111	103
indium	115	103
tin	118	103
antimony	121	103
barium	137	103
cerium*	140	
mercury	202	193(iridium)
thallium*	205	193
lead**	206	193
lead**	207	193
lead**	208	193

* This element is present in the tuning solution (A4.9).

** Lead is quantified from the sum of the intensities of these three mass isotopes to correct for different isotopic ratios arising in different geographical locations.

Internal standards are used to compensate for instrument drift, change in nebulisation efficiency from sample to sample and other physical effects arising from the sample matrix.

B The determination of selected elements in soils by *aqua regia* extraction using inductively coupled plasma-optical emission spectrometry

B1 Performance characteristics of method

B1.1	Substances determined	Aluminium, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, potassium, tin, titanium, vanadium and zinc.
B1.2	Type of sample	Contaminated land and soils.
B1.3	Basis of the method	Metals in the soil or contaminated land are extracted with <i>aqua regia</i> . The resulting solution is filtered, diluted and the metal concentration determined using ICP-OES.
B1.4	Range of application	Up to 1000 mg/kg for beryllium and manganese. Up to 2000 mg/kg for potassium and lithium. Up to 5000 mg/kg for arsenic, barium, calcium, cadmium, cobalt, chromium, copper, magnesium, molybdenum, nickel, lead, tin, titanium, vanadium and zinc. Up to 10000 mg/kg for aluminium and iron.
B1.5	Performance data	See Table B1.
B1.6	Interferences	<p>Spectral interferences should be minimised by the judicious selection of the appropriate analytical wavelength. Corrections for interferences may need to be made using interference correction algorithms supplied with instrument software. However, the validity of the corrections should be checked with the matrices analysed. This should be done whenever there is a change in the plasma conditions, when plasma torch maintenance is carried out, or when the rf generator is re-calibrated.</p> <p>Suitable positions for background correction should be selected by inspection of spectra for sample, standard, and blank extract solutions.</p> <p>Non-spectral interferences are primarily associated with matrix effects. These cause variations in solution viscosity and surface tension, which may cause significant variations in the nebulisation efficiency. Chemical interferences are of lesser significance. Where present, they</p>

should be compensated for by the use of matrix-matched standard and blank solutions.

B2 Principle

Metals are extracted from soil or contaminated samples with boiling *aqua regia*. The extraction solution is filtered and the concentration of metals in the filtrate determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

B3 Hazards

Appropriate personal protective equipment should be worn when handling reagents and potentially contaminated samples. Concentrated acids should always be added to water and operations carried out in a fume cupboard. Extract solutions contain concentrated acids and should be handled with care.

B4 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interference in the analysis. These should be checked for each batch of chemicals and reagents and verified by running reagent blanks with each batch of samples analysed. Reagents should be stored in tightly sealed containers or other suitable vessels, stored at room temperature, and kept in the dark, if necessary.

Water should be deionised (specific conductivity of less than 10 $\mu\text{S}/\text{cm}$) and volumetric glassware should be of at least grade B quality. All reagents should be appropriately labelled, including the expiry date. The preparation of all reagents should be recorded.

Unless otherwise stated, from the date of preparation all reagents may be stored at room temperature for up to one month.

B4.1 Concentrated nitric acid (SG 1.42).

B4.2 Concentrated hydrochloric acid (SG 1.16).

B4.3 Calibration blank solution. In a 1000-ml graduated beaker, add 70 ml of concentrated nitric acid (B4.1) to approximately 700 ml of water and mix well. To this solution, add 210 ml of concentrated hydrochloric acid (B4.2) and mix well. Make to 1000 ml with water.

B4.4 Mixed calibration standards. Mixed calibration standard solutions should be prepared using calibration blank solution (B4.3). For example, the following standard solutions may be suitable.

B4.4.1 Calibration standard solutions

Element	Concentration (mg/l)		
aluminium	5	10	20
barium	0.5	1	2
potassium	5	10	20

B4.4.2 Calibration standard solutions

Element	Concentration (mg/l)		
arsenic	5	10	20
beryllium	0.5	1	2
cadmium	1	2	4
calcium	5	10	20
chromium	2.5	5	10
cobalt	5	10	20
copper	1	2	4
iron	0.5	1	2
lead	5	10	20
lithium	5	10	20
magnesium	5	10	20
manganese	0.5	1	2
molybdenum	5	10	20
nickel	1	2	4
tin	5	10	20
titanium	5	10	20
vanadium	5	10	20
zinc	2.5	5	10

The following equation may be used for determining the volume of stock standard solution to be added

$$V_{\text{stock}} = (C_{\text{std}} \times V_{\text{std}}) / C_{\text{stock}}$$

Where

V_{stock} is the volume of the stock standard solution (ml);

V_{std} is the final volume of the calibration standard solution to be prepared (ml);

C_{stock} is the concentration of the stock standard solution requiring dilution (mg/l); and

C_{std} is the required concentration of the calibration standard solution (mg/l).

B4.5 Rinse solution. In a 1000-ml graduated beaker, add 50 ml of concentrated nitric acid (B4.1) to approximately 900 ml of water and mix well. Make to 1000 ml with water.

B4.6 Wash solution. In a 1000-ml graduated beaker, add 100 ml of concentrated nitric acid (B4.1) to approximately 900 ml of water and mix well. Make to 1000 ml with water.

B4.7 AQC check standard solutions. Two mixed AQC check standard solutions should be prepared in the calibration blank solution (B4.3). For example, the following standard solutions may be suitable.

B4.7.1 AQC check standard solution 1

Element	Concentration (mg/l)
aluminium	1
barium	1
potassium	10
silver	0.5

B4.7.2 AQC check standard solution 2

An AQC check standard solution containing each of the following elements, namely, arsenic, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, selenium, strontium, thallium, tin, titanium, vanadium and zinc should be prepared, each element at a concentration of 1 mg/l.

B5 Apparatus

Glassware should be washed using a detergent solution, for example Decon 90, and rinsed with water. The glassware should then be soaked in wash solution (B4.6) for a minimum of one hour. Glassware should then be rinsed with water, drained, and allowed to dry. In addition to normal laboratory glassware the following may be required.

B5.1 Volumetric flasks.

B5.2 Auto-pipettes.

B5.3 Inductively coupled plasma optical emission spectrometer equipped with a cross flow nebuliser, auto-sampler, and data handling system.

B5.4 Auto-sampler vials.

B5.5 Top pan balance capable of weighing to ± 0.01 g.

B5.6 Conical flasks: 150 ml.

B5.7 Dispensers: 2 – 10 ml.

B5.8 Filter funnels.

B5.9 Hardened filter papers (capable of fast flow rates): For example Whatman 541 filter papers, or equivalent.

B5.10 Hot-plate.

B5.11 Pump tubing.

B5.12 Gases: Argon, > 99.99 %.

B6 Sample preparation

Samples should be air-dried at a temperature not exceeding 30 °C and the loss on drying recorded. The air-dried sample should then be sieved over a 2 mm sieve. Material, other than stones, that is retained on the sieve should be crushed and ground to pass through the sieve. The mass of stones retained on the sieve should be recorded. Prior to analysis, crushed and ground material passing through the sieve should be thoroughly mixed and a representative sub-sample of material taken and ground to pass through a 425 μ m sieve.

B7 Analytical procedure

Step	Procedure	Note
B7.1	Weigh 1.0 g of prepared sample (B6) into a 100-ml conical flask. Cautiously, add 7 ml of concentrated nitric acid (B4.1) and 21 ml of concentrated hydrochloric acid (B4.2). Cover the flask with a watch glass and allow initial reactions to subside, see notes a and b	(a) Excessive frothing may be controlled by the addition of 2 - 3 drops of an anti foaming agent. (b) Appropriate blank and internal AQC samples should also be analysed.
B7.2	Gentle reflux the solution on a hot-plate for at least 3 hours, see note c.	(c) During the extraction process, no part of the flask base should be allowed to become dry. If necessary, remove the flask from the hot-plate, allow it and the contents to cool, and cautiously add 3 ml of concentrated nitric acid (B4.1) and 9 ml of concentrated hydrochloric acid (B4.2) to continue the extraction. If any part of the sample is allowed to boil dry the extraction process should be aborted and then repeated.
B7.3	Remove the flask from the hot-plate, and add 50 ml of water. Bring the resulting solution just to boiling point. Allow the solution to cool to room temperature. Quantitatively transfer the extract to a 100-ml volumetric flask. Make to 100 ml with water. Filter the solution (B5.9) and transfer the clear filtrate (see note d) to a plastic vial. The clear solution is now ready for ICP-OES determination.	(d) If the filtrate remains cloudy, filter the extract solution through a finer filter paper.
B7.4	Prior to analysis, set up and carry out system suitability checks (according to manufacturer's instructions) to verify the instrument performance.	
B7.5	Initial calibration should be carried out using calibration blank (B4.3) and calibration standard solutions (B4.4) see note e. Typical wavelengths monitored are shown in Table B2.	(e) The calibration may be checked using AQC solutions B4.7. Calibration should be checked at regular periods and at the end of the analysis.
B7.6	Analyse sample extracts, see note f. Between each sample, rinse the sampler introduction system with the rinse solution (B4.5).	(f) For samples with concentrations exceeding the range, the extract solution (B7.3) should be appropriately diluted with calibration blank solution (B4.3) and re-

analysed. Alternatively, consideration should be given to repeating the analysis using a smaller quantity of sample (B7.1) or using more *aqua regia* and making to a larger volume (B7.3).

B8 Calculations

The concentration of the analyte in the sample is given by

$$C_{\text{sample}} = (C_{\text{extract}} \times V_{\text{extract}} \times \text{DF}) / M_{\text{sample}}$$

Where C_{sample} is the concentration of the element in the air-dried sample (mg/kg);
 C_{extract} is the concentration of the element in the sample extract solution (mg/l);
 V_{extract} is the volume of extract (ml, usually 100 ml, section B7.3);
DF is the dilution factor, if any (note f, section B7.6); and
 m_{sample} is the mass of sample (g, usually 1 g, section B7.1).

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed. In addition, the reporting of results may also need to take into account whether results are calculated on an air-dried basis (for example at 30 °C) or on a dry weight basis (for example at 105 °C).

When an air-dried sample is prepared, and from this say A % of inert extraneous material is removed, then if (excluding inert extraneous material)

$$\text{moisture content on air-dried matter} = B \%$$

and

$$\text{metal concentration on air-dried matter} = C \text{ mg/kg}$$

then

$$\text{metal concentration on dry weight basis} = (C \times 100) / (100 - B) \text{ mg/kg}$$

If the inert extraneous material needs to be taken into account, then

$$\text{metal concentration on air-dried matter} = (C \times (100 - A)) / 100 \text{ mg/kg}$$

and

$$\text{metal concentration on dry weight basis} = ((C \times 100) / (100 - B)) \times ((100 - ((A \times 100) / (100 - B))) / 100) \text{ mg/kg}$$

Table B1 Performance data

Element	LOD (mg/kg)	Certified Reference Material								
		LGC 6135			LGC 6138			LGC 6139		
		CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)
aluminium	26	22700	6.0	36	14600	4.3	21			
arsenic	4	66	6.8	1.2	24	5.2	12.8	27	2.2	12.1
barium	2	134	10.0	5.9	62	19.8	274			
beryllium	0.1	1.4	2.3	21.0	1.5	3.8	15.0			
calcium	39	21900	2.8	-6.4	23100	2.7	-0.8			
cadmium	0.3							2.3	2.2	98
chromium	0.6	356	3.3	3.7	437	2.3	7.0	80	2.6	0.7
cobalt	0.6	20	1.9	-8.6	15	6.9	19.2			
copper	0.7	105	2.0	4.1	50	12.0	28	92	1.5	-0.1
iron	10	40900	7.1	-7.5	40400	3.0	-4.4			
lead	10	391	13.2	-3.0	220	44.9	12.2	160	1.8	-2.6
lithium	0.1	20	4.4	161	26	3.6	52			
magnesium	11	7000	2.0	2.1	5600	2.9	-5.0			
manganese	0.7	348	2.3	-6.4	567	3.1	-2.7			
molybdenum	4	20	15.1	4.9	14.7	1.4	13.4			
nickel	0.3	277	2.4	-3.4	133	9.5	58	38	1.8	-3.4
potassium	26	5100	10.6	79	2500	5.3	63			
tin	4	35	43	-36	23	33	-14.2			
titanium	0.8	200	26	93						
vanadium	0.2	78	7.4	21	76	3.0	14.4			
zinc	10	316	5.6	-1.9	146	8.4	2.7	513	2.2	-6.8

Performance data provided by Environmental Analysis Laboratories (EAL)

LOD is calculated (following analysis of 11 batches in duplicate) as 4.65 x within batch standard deviation determined from analysis of acid washed quartz analysed using the procedures described.

LGC 6135 is soil from a brick works site.

LGC 6138 is soil from a coal carbonisation site.

LGC 6139 is a river clay sediment.

Results with a high bias may indicate that the CRM value may need to be checked (for example total or extractable value and methodology used to generate the reference value) or that the procedure used for that element may be inappropriate for the determination of that element in the matrix.

Table B2 Typical wavelengths used

Element	Wavelength (nm)
aluminium	308.215
arsenic	188.979
barium	233.527
beryllium	313.102
calcium	317.933
cadmium	228.802
chromium	267.708
cobalt	230.786
copper	324.752
iron	273.955
lead	220.353
lithium	670.784
magnesium	285.213
manganese	257.610
molybdenum	202.031
nickel	231.604
potassium	766.490
strontium	460.733
tin	189.927
titanium	337.279
vanadium	292.402
zinc	206.197

All wavelengths are viewed axially.

C The determination of selected elements in soils by *aqua regia* extraction using inductively coupled plasma-optical emission spectrometry

C1 Performance characteristics of method

C1.1	Substances determined	Arsenic, antimony, barium, beryllium, cadmium, cobalt, copper, chromium, iron, lead, manganese, mercury, molybdenum, nickel, selenium, thallium, vanadium and zinc. Subject to validation, these procedures may also be used for the determination of boron, sulphur, phosphorus and other metallic elements.
C1.2	Type of sample	Contaminated land and soils.
C1.3	Basis of the method	Metals in soil or contaminated land are extracted with <i>aqua regia</i> . The resulting solution is diluted with water and the concentration of metals is determined using inductively coupled plasma optical emission spectrometry (ICP-OES).
C1.4	Range of application	Up to 60 mg/kg for mercury. Up to 1200 mg/kg for the other metals. The range may be extended by appropriate dilution of the resulting <i>aqua regia</i> extract.
C1.5	Performance data	See Table C1.
C1.6	Interferences	ICP-OES is prone to spectral interferences, see Introduction section. The instrument manufacturer may provide some information on likely interactions between spectral wavelengths.

C2 Principle

The sample of soil or contaminated land is extracted with hot *aqua regia*. The extract is cooled, diluted with water, and filtered, if necessary. The concentration of the metals in the extract is determined using ICP-OES against calibration standard solutions prepared in a similar matrix.

C3 Hazards

Appropriate personal protective equipment should be worn when handling reagents and potentially contaminated samples. Concentrated acids should always be added to water and operations carried out in a fume cupboard. The extract solutions contain concentrated acids and should be handled with care.

C4 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interference in the analysis. This should be checked for each batch of chemicals and reagents, and verified by running reagent blanks with each batch of samples analysed. Reagents should be stored in tightly sealed containers or other suitable vessels and stored at room temperature and kept in the dark, if necessary.

Water should be deionised (specific conductivity of less than 10 $\mu\text{S}/\text{cm}$) and volumetric glassware should be of at least grade B quality. All reagents should be appropriately labelled, including the expiry date of the reagent. The preparation of all reagents should be recorded.

C4.1 Concentrated nitric acid (SG 1.42).

C4.2 Concentrated hydrochloric acid (SG 1.18).

C4.3 *Aqua regia* diluent solution. To a 10-litre bottle, add approximately 5 litres of water. To the bottle, add 2 litres of concentrated hydrochloric acid (C4.2) and 750 ml of concentrated nitric acid (C4.1). Mix well and make to 10 litres with water. Mix well.

C4.4 Nitric acid rinse solution (0.5 v/v%). To a 5-litre bottle, add approximately 2.5 litres of water. To this bottle, add 25 ml of concentrated nitric acid (C4.1). Make to 5 litres with water and mix. (This solution should be pumped through the ICP system between analyses.)

C4.5 Mixed stock calibration solutions. A mixed stock solution containing arsenic, antimony, barium, beryllium, cadmium, cobalt, copper, chromium, iron, lead, manganese, molybdenum, nickel, selenium, thallium, vanadium and zinc, each at a concentration of 1000 mg/l. This solution is usually available commercially. A separate stock solution containing mercury at a concentration of 1000 mg/l should also be available.

C4.5.1 Mixed working calibration solution (5 mg/l). To a 1000-ml volumetric flask containing approximately 500 ml of water, add 5.0 ml of the mixed stock calibration solution (C4.5) and 200 ml of concentrated hydrochloric acid (C4.2) followed by 75 ml of concentrated nitric acid (C4.1). Mix well. Make to 1000 ml with water and mix. This solution may be stored in a plastic bottle at room temperature for up to 12 months.

C4.5.2 Mixed working calibration solution (10 mg/l). To a 1000-ml volumetric flask containing approximately 500 ml of water, add 10.0 ml of the mixed stock calibration solution (C4.5) and 200 ml of concentrated hydrochloric acid (C4.2) followed by 75 ml of concentrated nitric acid (C4.1). Mix well. Make to 1000 ml with water and mix. This solution may be stored in a plastic bottle at room temperature for up to 12 months.

C4.5.3 Mixed working calibration solution (20 mg/l). To a 1000-ml volumetric flask containing approximately 500 ml of water, add 20.0 ml of the mixed stock calibration solution (C4.5) and 200 ml of concentrated hydrochloric acid (C4.2) followed by 75 ml of concentrated nitric acid (C4.1). Mix well. Make to 1000 ml with water and mix. This solution may be stored in a plastic bottle at room temperature for up to 12 months.

C4.5.4 Mercury working calibration solution (0.25 mg/l). To a 1000-ml volumetric flask containing approximately 500 ml of water, add 0.25 ml of the mercury stock calibration solution (C4.5) and 200 ml of concentrated hydrochloric acid (C4.2) followed by 75 ml of concentrated nitric acid (C4.1). Mix well. Make to 1000 ml with water and mix. This solution may be stored in a plastic bottle at room temperature for up to 12 months.

C4.5.5 Mercury working calibration solution (0.5 mg/l). To a 1000-ml volumetric flask containing approximately 500 ml of water, add 0.5 ml of the mercury stock calibration solution (C4.5) and 200 ml of concentrated hydrochloric acid (C4.2) followed by 75 ml of concentrated nitric acid (C4.1). Mix well. Make to 1000 ml with water and mix. This solution may be stored in a plastic bottle at room temperature for up to 12 months.

C4.5.6 Mercury working calibration solution (1.0 mg/l). To a 1000-ml volumetric flask containing approximately 500 ml of water, add 1.0 ml of the mercury stock calibration solution (C4.5) and 200 ml of concentrated hydrochloric acid (C4.2) followed by 75 ml of concentrated nitric acid (C4.1). Mix well. Make to 1000 ml with water and mix. This solution may be stored in a plastic bottle at room temperature for up to 12 months.

C4.6 Mixed independent stock calibration solutions. These solutions are of the same concentrations as described in section C4.5. A mixed independent stock solution containing arsenic, antimony, barium, beryllium, cadmium, cobalt, copper, chromium, iron, lead, manganese, molybdenum, nickel, selenium, thallium, vanadium and zinc, each at a concentration of 1000 mg/l. This solution is usually available commercially. A separate independent stock solution containing mercury at a concentration of 1000 mg/l should also be available. These solutions may be stored in plastic bottles at room temperature for up to 12 months.

C4.6.1 Mixed independent working calibration solution (10 mg/l). To a 1000-ml volumetric flask containing approximately 500 ml of water, add 10.0 ml of the mixed independent stock calibration solution (C4.6). To this solution add, 200 ml of concentrated hydrochloric acid (C4.2) and 75 ml of concentrated nitric acid (C4.1). Mix well. Make to 1000 ml with water and mix. This solution may be stored in a plastic bottle at room temperature for up to 12 months.

C4.6.2 Independent mercury working calibration solution (0.5 mg/l). To a 1000-ml volumetric flask containing approximately 500 ml of water, add 0.5 ml of the independent mercury stock calibration solution (C4.6). To this solution add, 200 ml of concentrated hydrochloric acid (C4.2) and 75 ml of concentrated nitric acid (C4.1). Mix well. Make to 1000 ml with water and mix. This solution may be stored in a plastic bottle at room temperature for up to 12 months.

C4.7 Stock soil-spiking solutions. These solutions comprise individual solutions containing the metal to be determined (except mercury) each at a concentration of 10000 mg/l. These solutions may be stored in plastic bottles at room temperature for up to 12 months.

C4.7.1 Working soil-spiking solution. For example, to a 25-ml volumetric flask, add 1.0 ml of the independent mercury stock calibration solution (C4.6) and 2.0 ml of each of the stock soil-spiking solutions (C4.7). Mix well and make to 25 ml with water. This solution should be freshly prepared as required. The concentration of mercury in this solution is 40 mg/l and the concentration of each of the other metals is 800 mg/l. The maximum

number of elements that can be prepared in this way is 12. If more elements are required it will be necessary to prepare two solutions.

C5 Apparatus

In addition to general laboratory glassware and pipettes, the following equipment is required: -

- C5.1 Top pan balance capable of weighing to ± 0.01 g.
- C5.2 Disposable graduated plastic digestion tubes, for example, Gerhart tubes calibrated to 50 ml.
- C5.3 Small watch glasses to fit the disposable plastic digestion tubes (C5.2).
- C5.4 Screw caps to fit the disposable graduated plastic digestion tubes (C5.2).
- C5.5 Positive displacement filters (nominal pore size of 2 μm) to fit the disposable graduated plastic digestion tubes (C5.2).
- C5.6 Thermostatically controlled heating block, set at and capable of maintaining a temperature of 110 °C.
- C5.7 Dispensers suitable for concentrated acids.

C6 Sample preparation

Soil or contaminated land samples should be air-dried at less than 30 °C, for example by spreading a portion of the sample onto paper and leaving this on a drying rack overnight. After gently breaking up any lumps (for example with a pestle and mortar) the weight of material such as stones or other inert matter retained after passing the air-dried sample through a 2 mm sieve should be recorded. The material passing through the sieve should be ground to less than 425 μm for example using a ceramic pestle and mortar. If the sample consists of "fill-material" (for example stones, concrete and brick) chalk or other such material which does not pass through the 2 mm sieve, then the whole sample may be crushed prior to grinding. The fact that no material has been removed from the air-dried sample should then be recorded. The ground sample should then be stored in a plastic bag prior to analysis.

C7 Analytical procedure

Step	Procedure	Note
C7.1	Weigh out 1.0 g of the prepared air-dried and ground sample (C6) into a digestion tube (C5.2) see notes a and b.	(a) If results are to be reported on a dry weight basis (at 105 °C) rather than on an air-dried basis (for example at 30 °C) it will be necessary to determine the dry solids content (% DSC) on a separate portion of the prepared air-dried and ground sample (C6).

(b) Appropriate AQC (for example matrix certified reference material) and blank samples should also be analysed. If the soil matrix requires replicate spike testing to be carried out, add 1.0 ml of the working soil spiking solution (C4.7.1) to a number of replicate matrix samples.

C7.2 Carefully, add to the digestion tube (C5.2) 3.5 ml of concentrated nitric acid (C4.1) and 10.0 ml of concentrated hydrochloric acid (C4.2).

C7.3 Place the tube on the heating block (C5.6) and observe if any reactions take place within the first ten minutes, see note c. Once foaming has ceased, place a watch glass (C5.3) on each tube and leave for 90 minutes.

(c) If frothing occurs, remove the tube from the heating block, allow the contents of the tube to cool and the frothing to cease, then place the tube back on to the heating block. Tapping the tube gently will often help break down any foam.

C7.4 Remove the tube from the heating block, allow the contents to cool, then dilute to 50.0 ml with water. Cap (C5.4) the tube and mix thoroughly, see note d.

(d) Most samples will, on standing, settle to give a clear solution. If necessary, filter the suspension, for example using positive displacement (C5.5).

C7.5 Set up the ICP according to manufacturer's instructions using the wavelengths shown in Table C2.

C7.6 Calibrate the instrument using the mixed working calibration solutions (C4.5.1 - C4.5.4) and the *aqua regia* diluent solution (C4.3) see note e.

(e) Depending on the number of samples to be determined, it may be necessary to re-calibrate the instrument periodically.

C7.7 Analyse the sample extracts, including the mixed independent mixed working calibration solution (C4.6.1) and AQC and blank samples, see note f.

(f) For any sample extract giving a result outside of the calibration range, the extract solution (C7.4) should be diluted accordingly or consideration given to repeating the analysis using a smaller quantity of sample (C7.1) or using more *aqua regia* and making to a larger volume (C7.4).

C8 Calculations

The extract concentration (mg/l) should be converted to a concentration in air-dried sample (mg/kg) as follows:

$$C_{\text{air-dried}} = (S_{\text{concentration}} \times \text{DF} \times V_{\text{extract}}) / M_{\text{sample}}$$

where

$C_{\text{air-dried}}$ is the concentration of the metal in the air-dried sample (mg/kg);
 $S_{\text{concentration}}$ is the concentration of the metal in the sample extract solution (mg/l);
 DF is the dilution factor, if applicable (note f, section C7.7);
 V_{extract} is the extract volume (ml, usually 50 ml, section C7.4); and
 M_{sample} is the mass of sample (g, usually 1 g, section C7.1).

To convert to a concentration based on dry weight (at 105 °C)

$$C_{\text{dry weight}} = (C_{\text{air-dried}} \times 100) / \text{DSC} \quad (\text{mg/kg})$$

where

$C_{\text{dry weight}}$ is the concentration on dry weight basis (mg/kg)
 DSC is the dry solids content of the air-dried sample (% , note a, section C7.1).

Table C1 Performance data

Element	CRM-035-050			Certified Reference Material CRM-040-050			CRM-045-050			LOD (mg/kg)
	CRM value (mg/kg)	Bias (%)	Precision (% RSD)	CRM value (mg/kg)	Bias (%)	Precision (% RSD)	CRM value (mg/kg)	Bias (%)	Precision (% RSD)	
antimony	111	59	7.6	289	67	6.6				0.9
arsenic	473	4.5	5.5	327	-3.0	5.5	18.4	11.2	3.4	2
barium	265	-1.7	6.6	803	5.4	5.3				3
beryllium	87.4	-2.8	5	69.1	-7.4	4.6				0.3
cadmium	136	8.2	5.2	229	-0.1	4.6	1.61	1.6	2.9	0.1
chromium	151	4.1	5	152	-4.5	4.7	85.3	-8.5	3.4	0.3
cobalt	147	-2.6	4.9	76.7	-6.8	4.5	13.5	5.8	2.2	0.2
copper	107	-1.0	5.3	86.7	-4.9	4.2	122	-1.8	2.7	2
iron	8250	76	9.4	6830	36	8.1	8210	70	9.7	22
lead	82.8	-4.9	4.7	120	-6.1	4.1	42.8	-4.1	4.2	2
manganese	619	7.7	5.2	385	-0.4	4.4	292	13.4	2.8	0.6
mercury	9.95	83	12.3	37.7	5	7.3	0.795	-1.3	22.4	0.4
molybdenum	260	6.2	5.0	133	-2.8	3.8				2
nickel	99.1	-2.1	4.4	107	-4.1	4.0	199	-7.9	2.4	0.3
selenium	141	0.4	5.1	161	-0.3	4.5				0.9
thallium	136	8.6	3.7	79.4	2.3	3.8				0.9
vanadium	77.7	10.8	4.6	161	-5.6	4.1				0.1
zinc	303	8.1	5.7	334	-1.7	4.8	330	-2.3	3	0.8

Performance data provided by Scientific Analysis Laboratories Ltd

LOD is calculated (following analysis of 11 batches in duplicate) as 5.13 x within batch standard deviation determined from analysis of acid washed sand analysed using the procedures described.

CRM-035-050 is a dried homogenised sieved loamy sand.

CRM-040-050 is a dried homogenised sieved sandy loam.

CRM-045-050 is a dried homogenised sieved silty clay.

Results with a high bias may indicate that the CRM value may need to be checked (for example total or extractable value and methodology used to generate the reference value) or that the procedure used for that element may be inappropriate for the determination of that element in the matrix.

Table C2 Analytical wavelengths used

Element	Wavelength (nm)
antimony	206.834
arsenic	188.980
barium	230.424
beryllium	249.473
cadmium	228.802
chromium	267.716
cobalt	230.786
copper	217.895
iron	260.709
lead	220.353
mercury	184.887
manganese	259.372
molybdenum	201.512
nickel	231.604
selenium	196.026
thallium	190.794
vanadium	311.837
zinc	213.857

All wavelengths are axially orientated.

D The determination of selected elements in soils by *aqua regia* microwave digestion using inductively coupled plasma-mass spectrometry

D1 Performance characteristics of method

D1.1 Substances determined	Antimony, arsenic, boron, barium, beryllium, cadmium, chromium, cobalt, copper, lead, magnesium, manganese, mercury, molybdenum, nickel, potassium, selenium, sulphur, tin, vanadium, and zinc.
D1.2 Type of sample	Contaminated land and soils.
D1.3 Basis of the method	Metals in soil or contaminated land are digested with <i>aqua regia</i> under high temperature and pressure in a microwave oven. The resulting solution is diluted with water, filtered if necessary, and the concentration of metals is determined using inductively coupled plasma-mass spectrometry (ICP-MS).
D1.4 Range of application	Up to 4000 mg/kg for manganese and lead. Up to 500 mg/kg for all other elements.
D1.5 Performance data	See Tables D1 and D1.1.
D1.6 Interferences	Spectral interference can be caused by isobaric overlap, where two or more isotopes of different elements occur with the same mass. Formation of oxides and chlorides can cause interference due to molecular or polyatomic mass overlap with isotopes of interest. (See Table 2)

D2 Principle

The sample is digested with *aqua regia* in a microwave oven and the resulting solution is filtered if necessary, and diluted with water. Metal concentrations are determined using ICP-MS against calibration standard solutions similarly diluted.

D3 Hazards

Concentrated acids should always be added to water and operations carried out in a fume cupboard. The extract solutions contain concentrated acids and should be handled with care. *Aqua regia* is a concentrated acid mixture and is corrosive. Particular care should be taken to avoid contact with eyes, respiratory system and skin. Irrigate any splashes with plenty of water. Personal protective equipment should be worn when handling acids.

Some metals are extremely toxic, and all samples should therefore be regarded as potentially hazardous and treated with due care and attention. The ICP torch should never be viewed directly without protective eyewear being worn as potentially dangerous UV radiation may be emitted.

D4 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interference in the analysis. This should be checked for each batch of chemicals and reagents, and verified by running reagent blanks with each batch of samples analysed. Reagents should be stored in tightly sealed containers, for example plastic or other suitable vessels and stored at room temperature and kept in the dark, if necessary.

Water should be deionized (specific conductivity of less than 10 $\mu\text{S}/\text{cm}$) and glassware should be of at least grade B quality. All reagents should be appropriately labelled, including the expiry date of the reagent. The preparation of all reagents should be recorded.

D4.1 Concentrated nitric acid (S G 1.42).

D4.2 Concentrated hydrochloric acid (S G 1.18).

D4.3 *Aqua regia* rinse solution (2 v/v %). To a 5-litre container, add approximately 2.5 litres of water followed by 25 ml of concentrated nitric acid (D4.1) and 75 ml of concentrated hydrochloric acid (D4.2). Mix well and make to 5000 ml with water. This solution may be stored at room temperature for up to one week.

D4.4 *Aqua regia* dilution solution (10 v/v%). To a 100-ml volumetric flask add approximately 50 ml of water followed by 2.5 ml of concentrated nitric acid (D4.1) and 7.5 ml of concentrated hydrochloric acid (D4.2). Mix well and make to 100 ml with water. This solution should be prepared on the day of use.

D4.5 Stock standard solutions.

D4.5.1 Stock standard solutions. These individual metal solutions contain 10 mg/l of mercury, 1000 mg/l of barium, boron, gold, lead and manganese, and 10000 mg/l of magnesium, potassium and sulphur.

D4.5.2 Multi-element stock standard solution (100 mg/l). This solution contains antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, molybdenum, nickel, selenium, tin, vanadium and zinc, each at a concentration of 100 mg/l.

D4.6 Calibration standard solutions. A number of calibration standard solutions should be prepared. For example:

D4.6.1 Calibration standard solution 5. To a 200-ml plastic volumetric flask, add approximately 50 ml of water followed by 5 ml of concentrated nitric acid (D4.1) and 15 ml of concentrated hydrochloric acid (D4.2). Mix well, and add the following volumes of stock standard solutions (D4.5.1).

Stock standard solution (D4.5.1)	Volume of stock standard solution (D4.5.1) (ml)
gold	1.0
lead	4.0
magnesium	5.0
manganese	4.0
mercury	4.0
potassium	2.0
sulphur	2.0

Make to 200 ml with water and mix. This solution may be stored for up to one month at room temperature.

D4.6.2 Calibration standard solution 4. To a 100-ml plastic volumetric flask, add approximately 25 ml of water followed by 1.25 ml of concentrated nitric acid (D4.1) and 3.75 ml of concentrated hydrochloric acid (D4.2). Mix well, and add 50.0 ml of calibration standard solution 5 (D4.6.1) and 0.25 ml of gold stock standard solution (D4.5.1). Make to 100 ml with water and mix. This solution may be stored at room temperature for up to one month. (Gold is added to this solution (and other solutions) to matrix-match all calibration solutions at a concentration of 5 mg/l).

D4.6.3 Calibration standard solution 3. To a 100-ml plastic volumetric flask, add approximately 50 ml of water followed by 2.5 ml of concentrated nitric acid (D4.1) and 7.5 ml of concentrated hydrochloric acid (D4.2). Mix and add 2.5 ml of multi-element stock standard solution (D4.5.2) and the following volumes of stock standard solutions (D4.5.1).

Stock standard solution (D4.5.1)	Volume of stock standard solution (D4.5.1) (ml)
barium	0.25
boron	0.25
gold	0.50
mercury	0.25

Mix and make to 100 ml with water. This solution may be stored at room temperature for up to one month.

D4.6.4 Calibration standard solution 2. To a 100-ml plastic volumetric flask, add approximately 25 ml of water followed by 2 ml of concentrated nitric acid (D4.1) and 6 ml of concentrated hydrochloric acid (D4.2). Mix and add 20.0 ml of calibration standard 3 (D4.6.3) and 0.4 ml of gold stock standard solution (D4.5.1). Mix and make to 100 ml with water. This solution may be stored at room temperature for up to one month.

D4.6.5 Calibration standard solution 1. To a 100-ml plastic volumetric flask, add approximately 25 ml of water followed by 2 ml of concentrated nitric acid (D4.1) and 6 ml of concentrated hydrochloric acid (D4.2). Mix and add 20.0 ml of calibration standard 2 (D4.6.4) and 0.4 ml of gold stock standard solution (D4.5.1). Mix and make to 100 ml with water. This solution may be stored at room temperature for up to one month.

D4.7 AQC solutions. These solutions should be of the same concentrations as described in sections D4.5.1 and D4.5.2.

D4.7.1 AQC stock standard solutions. These individual metal solutions contain 10 mg/l of mercury, 1000 mg/l of barium, boron, gold, lead and manganese, and 10000 mg/l of magnesium, potassium and sulphur.

D4.7.2 Multi-element AQC stock standard solution (100 mg/l). This solution contains antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, molybdenum, nickel, selenium, tin, vanadium and zinc, each a concentration of 100 mg/l.

D4.7.3 Working AQC solution 1. To a 100-ml plastic volumetric flask, add approximately 50 ml of water followed by 2.5 ml of concentrated nitric acid (D4.1) and 7.5 ml of concentrated hydrochloric acid (D4.2). Mix and add 1.0 ml of multi-element AQC stock standard solution (D4.7.2) and the following volumes of AQC stock standard solutions (D4.7.1).

Stock standard solution (D4.7.1)	Volume of stock standard solution (D4.7.1) (ml)
barium	0.10
boron	0.10
gold	0.50
mercury	1.0

Mix and make to 100 ml with water. This solution may be stored at room temperature for up to one month.

D4.7.4 Working AQC solution 2. To a 100-ml plastic volumetric flask, add approximately 50 ml of water followed by 2.5 ml of concentrated nitric acid (D4.1) and 7.5 ml of concentrated hydrochloric acid (D4.2). Mix and add the following volumes of AQC stock standard solutions (D4.7.1).

Stock standard solution (D4.7.1)	Volume of stock standard solution (D4.7.1) (ml)
gold	0.50
lead	1.0
magnesium	1.0
manganese	1.0
potassium	0.50
sulphur	0.50

Mix and make to 100 ml with water. This solution may be stored at room temperature for up to one month.

D4.8 Intermediate set up stock standard solutions. These individual metal solutions contain 1000 mg/l of barium, beryllium, cadmium, cerium, copper, germanium, lead, magnesium, rhodium, scandium, terbium and thallium.

D4.8.1 Intermediate set up solution. To a 50-ml volumetric flask, add approximately 25 ml of water followed by 0.5 ml of concentrated nitric acid (D4.1). Mix and add 0.5 ml of each of the intermediate set up stock standard solutions (D4.8). Mix and make to 50 ml with water. This solution may be stored at room temperature for up to six months.

D4.8.2 Working set up solution. To a 1000-ml volumetric flask, add approximately 500 ml of water and 10 ml of concentrated nitric acid (D4.1). Mix and add 1.0 ml of the intermediate set up solution (D4.8.1). Mix and make to 1000 ml with water. This solution may be stored at room temperature for up to one month.

D4.9 Detector calibration solution. To a 50-ml volumetric flask, add approximately 25 ml of water and 4.0 ml of calibration standard solution 3 (D4.6.3). Mix and make to 50 ml with water. This solution may be stored at room temperature for up to one week.

D4.10 Stock internal standard solutions. These individual metal solutions contain 10 mg/l of rhodium and thulium and 1000 mg/l of gold.

D4.10.1 Internal standard solution. To a 1000-ml volumetric flask, add approximately 500 ml of water followed by 5 ml of concentrated nitric acid (D4.1) and 15 ml of concentrated hydrochloric acid (D4.2). Mix and add the following volumes of the stock internal standard solutions (D4.10).

Stock internal standard solutions (D4.10)	Volume of stock internal standard solutions (D4.10) (ml)
gold	5.0
rhodium	1.0
thulium	1.0

Mix and make to 1000 ml with water. This solution may be stored at room temperature for up to one week.

D5 Apparatus

Glassware should be washed using a detergent solution, for example Decon-90 or equivalent and rinsed with water. The glassware should then be soaked in acid solution, for example, 10 % nitric acid, for a minimum of one hour. Glassware should then be rinsed with water, drained, and allowed to dry.

D5.1 Volumetric flasks, various sizes.

D5.2 Variable pipettes, capable of dispensing 0.1-10 ml.

D5.3 Auto-sampler test tubes.

D5.4 Top pan balance capable of weighing 0.001 - 200 g.

D5.5 Microwave, capable of heating all samples to a temperature of 175 °C .

D5.6 Suitable microwave vessels with lids, capable of operating at approximately 150 psi.

D6 Sample preparation

Samples should be collected in plastic bags, bottles or pots, as appropriate. No special preservation is required but the samples should be refrigerated between 2 - 5 °C and analysed as soon as possible. Fill a large weighing boat with a representative sub-sample of the relevant soil or contaminated land. Place the boat into a drying cabinet maintained at a temperature not exceeding 40 °C. Leave for at least 24 hours or until dry. Grind the whole of this sub-sample so it passes through a 250 µm sieve. If the sub-sample contains stones or other objects that cannot be ground they should be removed, and the mass recorded. An appropriate description of the material removed should also be recorded.

D7 Analytical procedure

Step	Procedure	Note
D7.1	Accurately, weigh out 0.5 g of the ground soil or contaminated land sub-sample into a microwave vessel (D5.6). See note a. To the vessel, add 10.0 ml of water and 0.5 ml of gold stock standard solution (D4.5.1). To this mixture add, 2.5 ml of nitric acid (D4.1) and 7.5 ml of hydrochloric acid (D4.2). Mix cautiously, see note b.	(a) If samples are to be reported on a dry weight basis (at 105 °C) rather than on an air-dried basis, (for example at 30 °C or 40 °C) it will be necessary to carry out a dry solids content (%DSC) determination on a separate portion of the air-dried material. The result should be expressed as percent dried solids. (b) If effervescence occurs, allow the reaction to subside, before continuing.
D7.2	Cap the vessel and place in the microwave. Digest the solution for 35 minutes, ramping the temperature of the solution to 175 °C in the first 15 minutes and holding the temperature at 175 °C for the remaining 20 minutes. Allow the solution to cool to a safe temperature before opening the microwave. Remove the vessel from the microwave and allow the solution to cool to room temperature. See note c.	(c) The vessel may still be hot when removed from the microwave and should be handled with care. As the microwave vessel maybe under pressure; it should be opened safely in a fume cupboard.
D7.3	To the cooled solution, see note d, add approximately 20 ml of water and quantitatively transfer the contents to a suitable container, see note e. Rinse the vessel with 10 - 20 ml of water and add the washings to the container. Repeat as necessary. Make to 100.0 ml with water. The solution is now ready for ICP-MS determination.	(d) If the contents of the vessel appear suspect, for example excessive solution loss, it should be discarded and the analysis repeated. (e) If necessary, the digest solution should be filtered and the filter rinsed as appropriate.
D7.4	Blank solutions (D4.4) should be prepared, as should appropriate CRMs or in-house reference materials. These should be analysed using the procedures described in sections D7.1 - D7.3.	
D7.5	Set up the instrument according to the manufacturer's instructions and optimise as necessary using solutions D4.8, D4.8.1, D4.8.2 and D4.9.	
D7.6	Using the isotopic mass numbers shown in Table D2, analyse the calibration standard	(f) This is usually carried out on-line.

solutions (D4.6.1 - D4.6.5) and blank (D7.4) and sample (D7.3) solutions and any AQC solutions (D4.7 and D7.4). The internal standard solution (D4.10.1) should be aspirated with all the above solutions at a ratio of 5:1, see note f. Between each sample and standard solution determination, the rinse solution (D4.3) should be used to rinse the auto-sampler. See note g.

(g) For any sample solution giving a result outside of the calibration range, the extract solution (D7.3) should be diluted (D4.4) accordingly and re-analysed or consideration given to repeating the analysis using a smaller quantity of sample (D7.1) or using more *aqua regia* and making to a larger volume (D7.3).

D8 Calculations

The extract concentration (mg/l) should be converted to a concentration in air-dried sample (mg/kg) as follows:

$$C_{\text{air-dried}} = (S_{\text{concentration}} \times \text{DF} \times V_{\text{extract}}) / M_{\text{sample}}$$

where

$C_{\text{air-dried}}$ is the concentration of the metal in the air-dried sample (mg/kg);
 $S_{\text{concentration}}$ is the concentration of the metal in the sample extract solution (mg/l);
 DF is the dilution factor, if applicable (note g, section D7.6);
 V_{extract} is the extract volume (ml, usually 100 ml, section D7.3); and
 M_{sample} is the mass of sample (g, usually 0.5 g, section D7.1).

To convert to a concentration based on dry weight (for example at 105 °C)

$$C_{\text{dry weight}} = (C_{\text{air-dried}} \times 100) / \text{DSC} \quad (\text{mg/kg})$$

where

$C_{\text{dry weight}}$ is the concentration on dry weight basis (mg/kg)
 DSC is the dry solids content of the air-dried sample (% , note a, section D7.1).

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed. In addition, the reporting of results may also need to take into account whether results are calculated on an air-dried basis (for example at 30 °C) or on a dry weight basis (at 105 °C).

Table D1 Performance data

Element	LOD (mg/kg)	Certified Reference Material					
		CRM 7002 Sand			CRM 7003 Clay		
		CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)
barium	3	99.1	6.3	1.6	146		
beryllium	0.2	2.83			1.29	5.4	10.9
cadmium	0.2	0.28	5.4	9.4	0.32	4.7	-3.8
chromium	2	147	4.5	2.2	42.4		
cobalt	0.3	11.1	4.6	-4	10.3	4.2	-2.1
lead	1	35.5	3.9	8.6	25.2	4.3	9.6
manganese	5	531	2.8	-2.1	529	2.4	5.7
nickel	2	40.1	3.9	-0.6	28.8	3	2.9
zinc	10	64.0	6.2	-7.7	69.4		

Element	Certified Reference Material CRM 7004 Loam		
	CRM value (mg/kg)	RSD (%)	Bias (%)
beryllium	2.69	6.1	8.4
cadmium	1.44	4.5	6.6
chromium	46.3	5.5	3.2
cobalt	17.5	5.9	3.3
lead	83.1	3.3	5.2
manganese	741	4.0	2.8
nickel	30.4	4.3	6.9
zinc	198	3.7	3.7

Table D1.1 Performance data based on a spiked agricultural soil

Element	LOD (mg/kg)	Soil spiking value (mg/kg)	RSD (%)	Recovery (%)	Bias (%)
antimony	2	50	10.5	98.4	-1.6
arsenic	2	50	5	107.8	7.8
barium	3	50	6.3	101.6	1.6
beryllium	0.3	50	8.7	97.6	-2.4
boron	4	50	16.5	104.2	4.2
cadmium	0.2	50	4.5	106.6	6.6
chromium	2	100	9.8	100.4	0.4
cobalt	0.3	50	5.9	103.3	3.3
copper	2	100	8.5	105.8	5.8
lead	1	50	3.3	105.2	5.2
magnesium	410	10000	12.8	91.9	-8.1
manganese	5	1000	5.1	119.4	19.4
mercury	0.1	10	1.8	104.2	4.2
molybdenum	0.5	50	10.7	99.7	-0.3
nickel	2	100	4.3	106.9	6.9
potassium	30	1000	6.3	115.9	15.9
selenium	0.5	50	3.8	97.02	-2.98
sulphur	310	10000	11.5	96.9	-3.1
tin	0.3	50	4.8	112.6	12.6
vanadium	10	50	6.7	95.6	-4.4
zinc	10	100	9.2	98.4	-1.6

Data provided by Southern Water Scientific Services

LOD is calculated as 5 x within batch standard deviation of an agricultural soil, following analysis of 11 batches in duplicate.

CRM 7002 is a dried homogenised sieved sand soil to less than 100 µm.
 CRM 7003 is a dried homogenised sieved clay soil to less than 100 µm.
 CRM 7004 is a dried homogenised sieved loam soil to less than 100 µm.

Results with a high bias may indicate that the CRM value may need to be checked (for example total or extractable value and methodology used to generate the reference value) or that the procedure used for that element may be inappropriate for the determination of that element in the matrix.

Table D2 Elements and mass numbers monitored

Element	Mass	Internal standard
copper	63	103 (rhodium)
zinc	68	103
arsenic	75	103
selenium	82	103
beryllium	9	103
boron	11	103
sulphur	34	103
magnesium	24	103
potassium	39	103
vanadium	51	103
chromium	52	103
manganese	55	103
cobalt	59	103
nickel	60	103
molybdenum	95	103
cadmium	111	103
tin	120	103
antimony	121	103
mercury	202	169 (thulium)
lead	208	169
barium	138	169

Internal standards are used to compensate for instrument drift, change in nebulisation efficiency from sample to sample and other physical effects arising from the sample matrix.

E The determination of selected elements in soils by *aqua regia* extraction using inductively coupled plasma-optical emission spectrometry

E1 Performance characteristics of method

E1.1	Substances determined	Arsenic, barium, beryllium, cadmium, chromium, copper, lead, nickel, vanadium and zinc.
E1.2	Type of sample	Contaminated land and soils.
E1.3	Basis of the method	Metals in the soil or contaminated land are extracted with <i>aqua regia</i> . The resulting solution is filtered, diluted with water and the metal concentration determined using ICP-OES.
E1.4	Range of application	Up to 250 mg/kg for cadmium, Up to 500 mg/kg for arsenic, barium, beryllium and vanadium. Up to 1500 mg/kg for chromium, copper, nickel and zinc. Up to 2000 mg/kg for lead.
E1.5	Performance data	See Table E1.
E1.6	Interferences	<p>Spectral interferences should be minimised by the judicious selection of the appropriate analytical wavelength. Corrections for interferences may need to be made using interference correction algorithms (often supplied with instrument software). However, the validity of these corrections should be evaluated and checked with the matrix analysed. This may need to be carried out whenever there is a change in the plasma conditions, when plasma torch maintenance is carried out, or when the rf generator is re-calibrated.</p> <p>Suitable positions for background correction should be selected following inspection of spectral data for the sample, standard, and blank extract solutions.</p> <p>Non-spectral interferences are primarily associated with matrix effects. These cause variations in such physical properties as solution viscosity and surface tension, and may cause significant variations in the nebulization efficiency. Chemical interferences are of lesser significance, but when suspected should be compensated for by the use of matrix-matched solutions.</p>

E2 Principle

Metals are extracted from soil or contaminated samples with hot *aqua regia*. The extraction solution is filtered, diluted with water and the concentration of metals in the filtrate determined by ICP-OES.

E3 Hazards

Appropriate personal protective equipment should be worn when handling reagents and potentially contaminated samples. Concentrated acids should always be added to water and operations carried out in a fume cupboard. Extract solutions contain concentrated acids and should be handled with care.

E4 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interference in the analysis. These are checked for each batch of chemicals and reagents and verified by running reagent blanks with each batch of samples analysed. Reagents should be stored in tightly sealed containers for example dedicated high density polyethylene bottles or other suitable vessels, stored at room temperature, and kept in the dark, if necessary.

Water should be deionised (specific conductivity of less than 10 $\mu\text{S}/\text{cm}$) and volumetric glassware should be of at least grade B quality. All reagents should be appropriately labelled, including the expiry date. The preparation of all reagents should be recorded.

Unless otherwise stated, from the date of preparation, all reagents are stable for up to one month when stored at room temperature.

E4.1 Concentrated nitric acid (SG 1.42).

E4.2 Concentrated hydrochloric acid (SG 1.18).

E4.3 Calibration standard solutions. These individual metal solutions contain 1000 mg/l of arsenic and cadmium, and 10000 mg/l of barium, beryllium, chromium, copper, lead, nickel, vanadium and zinc.

E4.3.1 Intermediate calibration solution. To a 1000-ml volumetric flask, add 200 ml of water and 60 ml of concentrated hydrochloric acid (E4.2) followed by 20 ml of concentrated nitric acid (E4.1). Mix well and add 50.0 ml of the arsenic and cadmium calibration standard solutions (E4.3) and 20.0 ml of lead calibration standard solution (E4.3). To this solution add, 15.0 ml of the chromium, copper, nickel and zinc calibration standard solutions (E4.3) and 5.0 ml of the barium, beryllium and vanadium calibration standard solutions (E4.3). Mix well and make to 1000 ml with water. This solution may be stored at room temperature for up to six months.

E4.3.2 Working standard solution 1. To a 1000-ml volumetric flask, add 200 ml of water and 60 ml of concentrated hydrochloric acid (E4.2) followed by 20 ml of concentrated nitric acid (E4.1). Mix well and add 5.0 ml of intermediate calibration solution (E4.3.1). Mix well and make to 1000 ml with water. This solution may be stored at room temperature for up to two months.

E4.3.3 Working standard solution 2. To a 1000-ml volumetric flask, add 200 ml of water and 60 ml of concentrated hydrochloric acid (E4.2) and 20 ml of concentrated nitric acid (E4.1). Mix well and add 15.0 ml of intermediate calibration solution (E4.3.1). Mix well and make to 1000 ml with water. This solution may be stored at room temperature for up to two months.

E4.3.4 Working standard solution 3. To a 1000-ml volumetric flask, add 200 ml of water and 60 ml of concentrated hydrochloric acid (E4.2) and 20 ml of concentrated nitric acid (E4.1). Mix well and add 50.0 ml of intermediate calibration solution (E4.3.1). Mix well and make to 1000 ml with water. This solution may be stored at room temperature for up to two months.

E4.3.5 Working standard solution 4. To a 1000-ml volumetric flask, add 200 ml of water and 60 ml of concentrated hydrochloric acid (E4.2) and 20 ml of concentrated nitric acid (E4.1). Mix well and add 100.0 ml of intermediate calibration solution (E4.3.1). Mix well and make to 1000 ml with water. This solution may be stored at room temperature for up to two months.

E4.3.6 Blank calibration solution. To a 1000-ml volumetric flask, add 200 ml of water and 60 ml of concentrated hydrochloric acid (E4.2) followed by 20 ml of concentrated nitric acid (E4.1). Mix well and make to 1000 ml with water. This solution may be stored at room temperature for up to two months.

E4.4 Check calibration solutions. These solutions are of the same concentrations as described in section E4.3.

E4.4.1 Check calibration solutions. These individual metal solutions contain 10000 mg/l of arsenic, barium, beryllium, cadmium, chromium, copper, lead, nickel, vanadium and zinc.

E4.4.2 Intermediate AQC solution. To a 1000-ml volumetric flask, add 200 ml of water and 60 ml of concentrated hydrochloric acid (E4.2) and 20 ml of concentrated nitric acid (E4.1). Mix well and add 4.0 ml of the cadmium check calibration solution (E4.4.1) and 5.0 ml of the arsenic, barium, beryllium and vanadium check calibration solutions (E4.4.1). To this solution add, 6.0 ml of the zinc check calibration solution (E4.4.1) 10.0 ml of the chromium, copper and nickel check calibration solutions (E4.4.1) and 20.0 ml of the lead check calibration solution (E4.4.1). Mix well and make to 1000 ml with water. This solution may be stored at room temperature for up to two months.

E4.4.3 Working AQC solution. To a 1000-ml volumetric flask, add 200 ml of water and 60 ml of concentrated hydrochloric acid (E4.2) and 20 ml of concentrated nitric acid (E4.1). Mix well and add 50.0 ml of intermediate AQC solution (E4.4.2). Mix well and make to 1000 ml with water. This solution may be stored at room temperature for up to two months.

E5 Apparatus

Glassware should be washed using a detergent solution, for example Decon 90, and rinsed with water. The glassware should then be soaked in acid solution, for example 10 % nitric acid, for a minimum of one hour. Glassware should then be rinsed with water, drained, and allowed to dry. In addition to normal laboratory glassware the following may be required.

- E5.1 Volumetric flasks.
- E5.2 Pipettes.
- E5.3 Inductively coupled plasma atomic emission spectrometer equipped with an auto-sampler and data handling system.
- E5.4 Auto-sampler vials.
- E5.5 Top pan balance capable of weighing to ± 0.01 g.
- E5.6 Plastic extraction tubes and centrifuge tubes.
- E5.7 Dispensers.
- E5.8 Filter papers, Fisherbrand QT 270 or equivalent.
- E5.9 Heating block capable of maintaining a temperature of 120 °C

E6 Sample preparation

Samples should be air-dried for a minimum of 16 hours, crushed, and passed through a 425 μm sieve. They may be stored in air-tight containers at room temperature.

E7 Analytical procedure

Step	Procedure	Note
E7.1	Weigh 1.0 g of prepared sample (E6) into an extraction tube (E5.6). Cautiously, add 6 ml of concentrated hydrochloric acid (E4.2) and 2 ml of concentrated nitric acid (E4.1). Cover the tube with a watch glass and place it in a heating block at approximately 120 °C for 2 hours, see note a.	(a) Appropriate blank, CRM and internal AQC samples should also be analysed.
E7.2	Allow the solution to cool. Filter (E5.8) the solution into a 100 ml volumetric flask. Rinse the watch glass with water and allow the washings to pass through the filter paper. Ensure the filter paper and funnel are washed well with water. Make to volume with water. The solution is now ready for ICP-OES.	
E7.3	Prior to analysis, set up the ICP-OES according to manufacturer's instructions.	
E7.4	Calibration should be carried out using blank (E4.3.6) and calibration standard solutions (E4.3.2 - E4.3.5).	

E7.5 Analyse sample extract solution, see note b, and appropriate AQC solutions.

(b) For samples with concentrations exceeding the range, the extract solution (E7.2) should be appropriately diluted with calibration blank solution (E4.3.6) and re-analysed. Alternatively, consideration should be given to repeating the analysis using a smaller quantity of sample (E7.1) or using more *aqua regia* and making to a larger volume (E7.2).

E8 Calculations

The concentration of the element in the sample is given by:

$$C_{\text{sample}} = (C_{\text{extract}} \times V_{\text{extract}} \times \text{DF}) / M_{\text{sample}}$$

Where C_{sample} is the concentration of the element in the air-dried sample (mg/kg);
 C_{extract} is the concentration of element in the sample extract solution (mg/l);
 V_{extract} is the volume of extract (ml, usually 100 ml, section E7.2);
DF is the dilution factor, if any (note b, section E7.5); and
 M_{sample} is the mass of sample (g, usually 1 g, section E7.1).

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed. In addition, the reporting of results may also need to take into account whether results are calculated on an air-dried basis (for example at 30 °C) or on a dry weight basis (for example at 105 °C).

When an air-dried sample is prepared, and from this say A % of inert extraneous material is removed, then if (excluding inert extraneous material)

$$\text{moisture content on air-dried matter} = B \%$$

and

$$\text{metal concentration on air-dried matter} = C \text{ mg/kg}$$

then

$$\text{metal concentration on dry weight basis} = (C \times 100) / (100 - B) \text{ mg/kg}$$

If the inert extraneous material needs to be taken into account, then

$$\text{metal concentration on air-dried matter} = (C \times (100 - A)) / 100 \text{ mg/kg}$$

and

$$\text{metal concentration on dry weight basis} = ((C \times 100) / (100 - B)) \times ((100 - ((A \times 100) / (100 - B))) / 100) \text{ mg/kg}$$

Table E1 Performance data

Element	LOD (mg/kg)	Certified Reference Material								
		CRM 7001			CRM 7003			CRM 7004		
		CRM value (mg/kg)	Bias (%)	RSD (%)	CRM value (mg/kg)	Bias (%)	RSD (%)	CRM value (mg/kg)	Bias (%)	RSD (%)
arsenic	3	10.4	21.2	4.5	11.6	17.2	4.3	42.4	2.4	4.8
barium	3	108	-2.9	3	146	-4.6	2.5	217	-4.3	3.2
beryllium	3	1.02	11.3	3.4	1.29	12.4	3	2.69	14.7	8.1
cadmium	0.3	0.29	-11.7	10.2	0.32	-3.3	8.1	1.44	18	6.8
chromium	3	71.9	8.5	3.2	42.4	8.4	2.8	46.3	7.1	4
copper	3	28.9	10.9	4.0	25.4	10.0	3.5	167	5.2	3.6
lead	3	24.1	15.3	3.7	25.2	6.3	3.7	83.1	4.7	4.1
nickel	3	31.8	1.6	3.0	28.8	2.6	2.5	30.4	3.7	4.1
vanadium	3	52	-0.1	2.8	52.9	-0.9	2.1	95.1	-5.4	3.0
zinc	5	108	-0.7	3	69.4	0.8	3.2	198	2.1	3.8

Performance data provided by WSP Environmental.

LOD is calculated as 4.65 x the standard deviation of the calibration blank solution following extraction and analysis of 11 batches in duplicate.

CRM 7001 is a dried homogenised sieved light sandy soil to less than 100 µm.

CRM 7003 is a dried homogenised sieved silty clay soil to less than 100 µm.

CRM 7004 is a dried homogenised sieved loam soil to less than 100 µm.

Results with a high bias may indicate that the CRM value may need to be checked (for example total or extractable value and methodology used to generate the reference value) or that the procedure used for that element may be inappropriate for the determination of that element in the matrix.

Table E2 Typical wavelengths used

Element	Wavelength (nm)*
arsenic	189.0
barium	455.4
beryllium	313.0
cadmium	228.8
chromium	205.6
copper	324.8
lead	220.4
nickel	231.6
vanadium	290.9
zinc	206.2

* All wavelengths are axial except for the copper wavelength which is radial.

F The determination of selected elements in soils by *aqua regia* extraction using inductively coupled optical emission spectrometry

F1 Performance characteristics of method

F1.1	Substances determined	Arsenic, aluminium, barium, beryllium, cadmium, cobalt, copper, chromium, iron, lead, manganese, magnesium, molybdenum, nickel, vanadium, titanium and zinc.
F1.2	Type of sample	Contaminated land and soils.
F1.3	Basis of the method	Metals contained within the soil or contaminated land are extracted with <i>aqua regia</i> . The concentration of the metals in the resulting solution is quantified using ICP-OES.
F1.4	Range of application	Up to 50000 mg/kg for aluminium. Up to 250 mg/kg for cadmium. Up to 500 mg/kg for arsenic, beryllium, cobalt, chromium, molybdenum, nickel and vanadium. Up to 2500 mg/kg for lead. Up to 20000 mg/kg for magnesium. Up to 1000 mg/kg for titanium. Up to 5000 mg/kg for barium, copper, manganese and zinc. Up to 70000 mg/kg for iron.
F1.5	Performance data	See Table F1.
F1.6	Interferences	Spectral interferences can be avoided by careful selection of wavelength.

F2 Principle

Metals are extracted from soil samples following the addition of *aqua regia* and heating in test tubes in a heating block. The resulting solution is filtered, made to a known volume with water and the concentration of extracted metals quantified using ICP-OES.

F3 Hazards

Appropriate personal protective equipment should be worn when handling reagents and potentially contaminated samples. Concentrated acids should always be added to water and operations carried out in a fume cupboard. The extract solutions contain concentrated acids and should be handled with care.

F4 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interference in the analysis. This should be checked for each batch of chemicals and reagents and verified by running reagent blanks with each batch of samples analysed. Reagents should be stored in tightly sealed containers or other suitable vessels and stored at room temperature and kept in the dark, if necessary.

Water should be deionised (specific conductivity of less than 10 $\mu\text{S}/\text{cm}$), and volumetric glassware should be of at least uncertified grade A quality. All reagents should be appropriately labelled, including the expiry date of the reagent. The preparation of all reagents should be recorded.

F4.1 Concentrated nitric acid (SG 1.42).

F4.2 Concentrated hydrochloric acid (SG 1.18).

F4.3 Acid blank solution. Add 420 ml of concentrated hydrochloric acid (F4.2) to a 2 litre volumetric flask containing approximately 1400 ml of water. Mix well. Add 140 ml of concentrated nitric acid (A4.1) and mix well. Allow the solution to cool then make to 2000 ml with water. Mix well and transfer to a suitable container. This solution may be stored at room temperature for up to one week.

F4.4 Mixed stock calibration standard solutions. For example, the following mixed stock solutions should be prepared from individual standard solutions of known concentration. Alternatively, these may be commercially available.

F4.4.1 Stock calibration standard solution 1

Element	Concentration (mg/l)
arsenic	50
cadmium	25
chromium	50
copper	500
iron	7000
nickel	50
lead	250
zinc	500

F4.4.2 Stock calibration standard solution 2

Element	Concentration (mg/l)
aluminium	5000
barium	500
beryllium	50
cobalt	50
magnesium	2000
manganese	500
molybdenum	50
vanadium	50
titanium	100

The following equation may be used for determining the volume of stock standard solution to be added

$$V_{\text{stock}} = (C_{\text{std}} \times V_{\text{std}}) / C_{\text{stock}}$$

Where

V_{stock} is the volume of the stock standard solution (ml);

V_{std} is the final volume of the calibration standard solution to be prepared (ml);

C_{stock} is the concentration of the stock standard solution requiring dilution (mg/l); and

C_{std} is the required concentration of the calibration standard solution (mg/l).

F4.5 Working calibration standard solutions. Working calibration standard solutions should be prepared from stock calibration standard solutions F4.4.1 and F4.4.2. For example, five calibrations should be prepared in separate 500-ml volumetric flasks. To each flask, add approximately 300 ml of water and 105 ml of concentrated hydrochloric acid (A4.2) followed by 35 ml of concentrated nitric acid (A4.1). Mix well. To each flask add the appropriate volumes of the stock calibration standard solutions F4.4.1 and F4.4.2.

Working calibration solution	Volume of stock calibration standard solution 1 (F4.4.1) (ml)	Volume of stock calibration standard solution 2 (F4.4.2) (ml)
5	50.0	50.0
4	40.0	40.0
3	30.0	30.0
2	20.0	20.0
1	10.0	10.0

Make to 500 ml with water and mix well. A reagent blank solution should also be prepared. These solutions may be stored at room temperature for up to one month.

F4.6 Silicone anti-foaming agent (10 % v/v). Add 100 ml of anti-foaming agent to a 1 litre volumetric flask. Make to 1000 ml with water and mix well. This solution may be stored at room temperature for up to three months.

F5 Apparatus

Glassware should be washed using a detergent solution, for example Decon-90 or equivalent and rinsed with water. The glassware should then be soaked in acid solution, for example, 10 % nitric acid, for a minimum of one hour. Glassware should then be rinsed with water, drained, and dried in an oven at 100 °C.

F5.1 Volumetric flasks, various sizes, for example 500 ml, 1 litre and 2 litres.

F5.2 Pipettes: various sizes, for example 10, 20,30, 40 and 50 ml.

F5.3 ICP optical emission spectrometer with a quartz cyclonic spray chamber and gemcone nebuliser.

F5.4 Test tubes, 24 x2 00 mm of Pyrex or similar quality.

F5.5 Top pan balance capable of weighing to ± 0.01 g.

F5.6 Wide mouth glass bottles, 100ml.

- F5.7 Graphite block, suitably bored to hold the test tubes.
- F5.8 Dispensers, various sizes, for example 2 - 25 ml.
- F5.9 Filter funnels, polypropylene or similar quality.
- F5.10 Filter paper, Whatman 542, or equivalent.
- F5.11 Thermostatically controlled hot-plate capable of maintaining a temperature of 100 °C.
- F5.12 Gases: Argon, >99.99 %.

F6 Sample preparation

A representative portion of the as received sample should be weighed and air-dried at a temperature not exceeding 30 °C. The air-dried portion should be weighed and the moisture content determined. Inert material (for example stones etc) may be removed and the portion weighed again to determine the amount of inert material removed. The remaining material is crushed and ground to pass a 2 mm sieve.

F7 Analytical procedure

Step	Procedure	Notes
F7.1	Weigh out 1.0 g of the prepared soil or contaminated land sample (F6) into a test tube (F5.4). Carefully, add 7.0 ml of concentrated nitric acid (F4.1) followed by 21 ml of concentrated hydrochloric acid (F4.2) and 2 ml of anti-foaming agent (F4.6). Carefully, mix well.	
F7.2	Allow the tube to stand at room temperature for 15 minutes, then place the tube into the heating block on the pre-heated hot-plate at a temperature of 100 °C. Observe the reaction for several minutes, see note a.	(a) If the reaction becomes too vigorous and effervesces, add a small amount of water, mix well and continue.
F7.3	Gently heat the contents of the tube for 180 minutes. Allow the tube to cool slightly and remove it from the heating block. Allow the tube to cool to room temperature.	
F7.4	Filter the cooled extract solution through a filter paper (F5.10) into a 100-ml volumetric flask. Rinse the test tube with water and filter the rinsings through the filter paper into the flask. Make to 100 ml with water.	

F7.5 A reagent blank should also be prepared using the procedures described in sections F7.1 - F7.4 but without the soil. In addition, an AQC soil sample should be treated similarly.

F7.6 Following manufacturer's instructions, optimise the ICP-OES system using wavelengths shown in Table F2. The calibration solutions (F4.5) should then be analysed along with the blank and AQC samples, and the extracted sample solutions, see note b.

(b) If the result obtained for a particular element is greater than the range of application (F1.4) then the sample extract (F7.4) should be diluted using acid blank solution (F4.3) and re-analysed. Alternatively, the analysis should be repeated using a smaller quantity of sample (F7.1) or using more *aqua regia* and making to a larger volume (F7.4).

F8 Calculations

The concentration of the element in the sample is given by:

$$C_{\text{sample}} = (C_{\text{extract}} \times V_{\text{extract}} \times \text{DF}) / M_{\text{sample}}$$

Where C_{sample} is the concentration of the element in the air-dried sample (mg/kg);
 C_{extract} is the concentration of element in the sample extract solution (mg/l);
 V_{extract} is the volume of extract (ml, usually 100 ml, section F7.4);
 DF is the dilution factor, if any (note b, section F7.6); and
 M_{sample} is the mass of sample (g, usually 1 g, section F7.1).

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed. In addition, the reporting of results may also need to take into account whether results are calculated on an air-dried basis (for example at 30 °C) or on a dry weight basis (for example at 105 °C).

When an air-dried sample is prepared, and from this say A % of inert extraneous material is removed, then if (excluding inert extraneous material)

$$\text{moisture content on air-dried matter} = B \%$$

and

$$\text{metal concentration on air-dried matter} = C \text{ mg/kg}$$

then

$$\text{metal concentration on dry weight basis} = (C \times 100) / (100 - B) \text{ mg/kg}$$

If the inert extraneous material needs to be taken into account, then

metal concentration on air-dried matter = $(C \times (100-A))/100$ mg/kg

and

metal concentration on dry weight basis = $((C \times 100)/(100-B)) \times ((100 - ((A \times 100)/(100-B)))/100)$ mg/kg

Table F1 Performance data

Element	LOD (mg/kg)	Certified Reference Material								
		CRM 008-050			CRM 020-050			CRM 021-050		
		CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)
aluminium	3	23906	9.8	-21.2	1755	7.6	-20.7	2725.2	7.9	-13.2
arsenic	4	14.1	5.9	11.0	400	4.2	-4.4			
barium	0.2	53.6	6.2	-12.8	24.8	9.1	-7.7	586.4	5	-6.9
beryllium	0.2	1.07	7.8	-3.3						
cadmium	0.1				15.4	6.9	-1.4			
chromium	0.2	48.1	5.6	7.9						
cobalt	0.2	11.2	6.6	1.7	4.51	10.2	-9.4			
copper	0.3	36.4	3.7	-3.3	729	5.8	2.7			
iron	36	33042	4.1	-2.4	191706	5.7	-5.5			
lead	2	95.3	8.9	11.7						
magnesium	5	6741.8	4.2	-6.8	2687	5	-1.9	2637.4	5.9	0.1
manganese	0.2	260.8	4.5	-6.8	945	5.1	-7.8			
molybdenum	0.4	1.84	14.4	-8.0						
nickel	0.6	26.0	4.2	2.1	16.9	9.1	-2.1			
titanium	0.3									
vanadium	0.2	44.4	7.1	-4.4	6.47	5.8	0.4			
zinc	2	133.5	5.3	-0.5	3011	6.7	-5.7			

Element	Certified Reference Material								
	CRM 026-050			CRM 027-050			CRM 024-050		
	CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)
aluminium	17730	10.7	-9.3	8537	4.5	-0.8	8681	10.4	-19.3
arsenic	5.41			12.4	7.9	7.4			
barium	214	7.7	-5.9	166	5.2	-6.6	79.6	5.8	-7.9
beryllium	18.0	6.0	-9.5	2.73	7.5	-5.5			
cadmium	11.7	6.7	5.2	12.0	4.8	5.6			
chromium	27.2	9.7	1.0	26.9	5.3	8.7			
cobalt	6.77	5.9	10.5	4.70	5.5	9.7			
copper	18.8	5.3	-0.1	9.87	5.7	6.0			
iron	21906	6.1	2.3	11173	6.2	16			
lead				51.9	3.8	6.8			
magnesium	2837	8.8	1.1	2755	5.2	0.3	2945	5.5	-5.1
manganese	633	4.0	-5.5	259	6.1	-1.3	199	4.9	-1.6
nickel	14.4	7.1	-5.2	10.5	5.7	9.6			
vanadium	32.0	7.6	10	21.4	6.4	10.8	20.8	6.9	4.9
zinc	140	8	4.1	51.3	9.0	3.4			

Element	Certified Reference Material								
	CRM 032-050			CRM 036-050			CRM 037-050		
	CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)
aluminium	2470	6.7	33.1	5320	8.7	30.3	18500	7.0	16.6
arsenic	369	4.7	7.5	148	6.7	4.4	73.0	4.1	4.8
barium	122	9.9	13.2	61.4	6.4	12.7	354	7	12.8
beryllium	140	5.0	9.4	5.38	7.3	6.5	99.2	4.9	1
cadmium	131	4.8	2.9				91.7	5.5	20.1
chromium	15.0	37.3	5.1	41.0	5.4	12.7	118	4.5	12.5
cobalt	103	6.1	0.6	67.1	5.9	15.8	72.1	4.6	12.1
copper	585	7.4	5.4	66.4	5.7	2.2	129	5.0	2.1
iron				8210	6.7	39.4	14300	4.8	14
lead				132	7.1	15.2	118	4.7	25.4
magnesium	2540	6.1	34.9	2590	5.3	12.9	4590	4.6	2.3
manganese	1130	5.2	5.5	138	9.3	5.7	560	4.2	0.9
molybdenum	79.4	4.0	10.3	87.4	6	11.8	76.5	6.2	9.5
nickel	14.8	5.9	1.0	119	6	15.4	289	4.4	11.7
titanium							388	6.6	43.8
vanadium	9.38	5.8	18.3	23.3	6.8	38.6	86.9	4.4	11.9
zinc	2580	7.2	11.2	182	6.6	1.8	403	4.7	0.2

Element	Certified Reference Material								
	CRM 038-050			CRM 039-050			CRM 042-050		
	CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)
aluminium	15100	8.1	2.7	17600	6.8	20.3	16700	8.1	14.1
arsenic	25.0	10	4				265	10.4	8.3
barium	324	6.7	2.8	1010	4.4	4.8	763	4.9	1.9
beryllium	257	6.3	3	53.9	5.1	0.4	129	5.4	8
cadmium	87.0	5.8	14.1	265	4.8	0.6			
chromium	129	5.6	10.1	165	4.1	1.3	268	4.8	8.5
cobalt	84.7	5.8	15.5	123	4.6	5.8	168	4.8	10.2
copper	115	5.8	0.5	171	4.8	8.9	128	4.8	3.5
iron	12800	7.4	13.4	13300	3.8	6	12900	5.7	10.6
lead	128	6.2	15.3	178	4.4	3.9	182	5.1	9.1
magnesium	3670	5.6	0.2	4840	4.3	10.8	3830	5.8	2.8
manganese	506	6.3	3.7	372	4.7	4.9	594	4.9	0.9
molybdenum	311	6.8	0.7	171	5.3	1.5	104	6.2	19.8
nickel	131	5.8	12.8	206	4.2	2.7	130	4.8	12.6
titanium	412	8.5	20.6	413	7.6	10	435	9.6	16.6
vanadium	88.8	5.6	9.7	165	4.3	2	139	4.7	8.1
zinc	476	6.1	1.8	374	5.4	13.2	529	5.5	3.9

Element	Certified Reference Material								
	CRM 044-050			CRM 045-050			CRM 046-050		
	CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)	CRM value (mg/kg)	RSD (%)	Bias (%)
arsenic				18.4	8.4	0	7.47	15.3	10.8
cadmium	70.1	5.5	2.1	1.61	13.1	8.1	7.01	3.9	9.1
chromium	87.8	4.9	8.9	85.3	3.0	0.1	45.7	2.9	0.2
copper	63.7	5.8	20.5	122	0.4	4.5	62.2	2.9	12.9
cobalt	50.6	6.2	7.7	13.5	3.6	2.2	8.22	6.5	33.2
lead	75.9	4.9	25.7	42.8	14	21.7	45.3	7.4	25.8
manganese	204	4.8	13.9	292	3.4	1.5	118	4.3	18.1
nickel	87.0	4.8	9.9	199	3.3	2.5	37.5		
zinc	132	5.2	34.4	330	8	11.3	114	4.7	28.5

Performance data provided by STL.

LOD is calculated as 5 x within batch standard deviation of reagent blank extract solutions following analysis of 11 batches in duplicate.

- CRM-008-050 is a dried homogenised sieved soil/ sediment.
- CRM-020-050 is a dried homogenised sieved sandy loam.
- CRM-021-050 is a dried homogenised sieved sandy loam.
- CRM-024-050 is a dried homogenised sieved sandy loam.
- CRM-026-050 is a dried homogenised sieved sandy loam.
- CRM-027-050 is a dried homogenised sieved sandy loam.
- CRM-032-050 is a dried homogenised sieved sandy loam.
- CRM-036-050 is a dried homogenised sieved loamy sand.
- CRM-037-050 is a dried homogenised sieved sandy loam.
- CRM-038-050 is a dried homogenised sieved loam.
- CRM-039-050 is a dried homogenised sieved loam.
- CRM-042-050 is a dried homogenised sieved loam.
- CRM-044-050 is a dried homogenised sieved silt loam.
- CRM-045-050 is a dried homogenised sieved silt clay.
- CRM-046-050 is a dried homogenised sieved clay.

Results with a high bias may indicate that the CRM value may need to be checked (for example total or extractable value and methodology used to generate the reference value) or that the procedure used for that element may be inappropriate for the determination of that element in the matrix.

Table F2 Elements and wavelengths monitored

Element	Wavelength (nm)
aluminium	396.153
arsenic	188.984
barium	493.408
beryllium	313.107
cadmium	228.802
chromium	267.716
cobalt	228.616
copper	327.393
iron	273.955
lead	220.350
magnesium	279.077
manganese	257.610
molybdenum	202.031
nickel	231.604
titanium	334.940
vanadium	292.402
zinc	206.200

Iron is measured using radial orientation, and all other wavelengths are measured using axial orientation.

G The determination of mercury in soils by *aqua regia* extraction using cold vapour atomic fluorescence spectrometry

G1 Performance characteristics of method

G1.1	Substances determined	Mercury.
G1.2	Type of sample	Contaminated land and soils.
G1.3	Basis of the method	Mercury contained within the soil or contaminated land is extracted with <i>aqua regia</i> . The resulting solution is diluted with nitric acid and quantification is determined using cold vapour atomic fluorescence spectrometry. (Apart from the end detection technique, the analytical procedures described in this method are the same as those described in section A7).
G1.4	Range of application	Up to 2.5 mg/kg. The range may be extended by dilution of the extract.
G1.5	Performance data	See Table G1.
G1.6	Interferences	Oxidising species reduce the signal intensity.

G2 Principle

The sample of soil or contaminated land is extracted with *aqua regia* under reflux conditions. The extract is cooled and filtered, and the resulting solution diluted with water to matrix match the extracts to the standard solutions. Mercury concentrations are determined against calibration standard solutions, using reduction with tin chloride and cold vapour atomic fluorescence spectrometry. The resulting fluorescence is quantified at 254 nm.

G3 Hazards

Appropriate personal protective equipment should be worn when handling reagents and potentially contaminated samples. Concentrated acids should always be added to water and operations carried out in a fume cupboard. The extract solutions contain concentrated acids and should be handled with care.

G4 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interference in the analysis. This should be checked for each batch of chemicals and reagents and verified by running reagent blanks with each batch of samples analysed. Reagents should be stored in tightly sealed containers or other suitable vessels and stored at room temperature and kept in the dark, if necessary.

Water should be deionised (specific conductivity of less than 10 $\mu\text{S}/\text{cm}$) and volumetric glassware should be of at least grade B quality. All reagents should be appropriately labelled, including the expiry date of the reagent. The preparation of all reagents should be recorded.

G4.1 Concentrated nitric acid (SG 1.42).

G4.2 Concentrated hydrochloric acid (SG 1.18).

G4.3 Nitric acid / potassium dichromate solution. Add 12.5 g of potassium dichromate to a 1000-ml plastic bottle and add 500 ml of water. Stopper and mix well to dissolve the potassium dichromate. Carefully, add 500 ml of concentrated nitric acid (G4.1) to the dichromate solution. Stopper and mix well. This reagent may be stored at room temperature and kept for up to six months.

G4.4 Tin(II) chloride solution. Add 20 g of stannous chloride dihydrate to a 1000-ml glass bottle. Carefully, add 150 ml of concentrated hydrochloric acid (G4.2) and swirl to dissolve the dihydrate. Add 850 ml of water and mix carefully. Purify this reagent before use by passing air through the solution for at least 15 minutes to remove any traces of mercury. This reagent should be prepared on the day of use.

G4.5 *Aqua regia* instrument wash solution. Add 2700 ml of water to a 3000-ml plastic bottle. Carefully, add 75 ml of concentrated nitric acid (G4.1) and 225 ml of concentrated hydrochloric acid (G4.2). Shake to mix. This reagent may be stored at room temperature and kept for up to two weeks.

G4.6 Standard solution preparations. All standard solutions should be stored in plastic bottles and kept at room temperature. Stock standard solutions are commercially available.

G4.6.1 Intermediate calibration solution A (100 mg/l of Hg). To a 100-ml volumetric flask, add approximately 50 ml of water, 2 ml of nitric acid / potassium dichromate solution (G4.3) and 10.0 ml of 1000 mg/l mercury standard solution. Make to 100 ml with water and mix. This reagent may be stored at room temperature and kept for up to three months.

G4.6.2 Intermediate calibration solution B (1 mg/l of Hg). To a 1000-ml volumetric flask, add approximately 500 ml of water, 20 ml of nitric acid / potassium dichromate solution (G4.3) and 10.0 ml of intermediate calibration solution A (G4.6.1). Make to 1000 ml with water and mix. This reagent may be stored at room temperature and kept for up to one month.

G4.6.3 Blank calibration solution. To a 1000-ml volumetric flask, add approximately 500 ml of water, 25 ml of concentrated nitric acid (G4.1) and 75 ml of concentrated hydrochloric acid (G4.2). Make to 1000 ml with water and mix. This reagent may be stored at room temperature and kept for up to two weeks.

G4.6.4 Working calibration solution 2 (5 $\mu\text{g}/\text{l}$ of Hg). To a 1000-ml volumetric flask, add approximately 500 ml of water, 25 ml of concentrated nitric acid (G4.1) and 75 ml of concentrated hydrochloric acid (G4.2). Add 5.0 ml of intermediate calibration solution B (G4.6.2). Make to 1000 ml with water and mix. This reagent may be stored at room temperature and kept for up to two weeks.

G4.6.5 Working calibration solution 3 (10 µg/l of Hg). To a 1000-ml volumetric flask, add approximately 500 ml of water, 25 ml of concentrated nitric acid (G4.1) and 75 ml of concentrated hydrochloric acid (G4.2). Add 10.0 ml of intermediate calibration solution B (G4.6.2). Make to 1000 ml with water and mix. This reagent may be stored at room temperature and kept for up to two weeks.

G4.6.6 Working calibration solution 4 (15 µg/l of Hg). To a 1000-ml volumetric flask, add approximately 500 ml of water, 25 ml of concentrated nitric acid (G4.1) and 75 ml of concentrated hydrochloric acid (G4.2). Add 15.0 ml of intermediate calibration solution B (G4.6.2). Make to 1000 ml with water and mix. This reagent may be stored at room temperature and kept for up to two weeks.

G4.6.7 Working calibration solution 5 (20 µg/l of Hg). To a 1000-ml volumetric flask, add approximately 500 ml of water, 25 ml of concentrated nitric acid (G4.1) and 75 ml of concentrated hydrochloric acid (G4.2). Add 20.0 ml of intermediate calibration solution B (G4.6.2). Make to 1000 ml with water and mix. This reagent may be stored at room temperature and kept for up to two weeks.

G4.6.8 Working calibration solution 6 (25 µg/l of Hg). To a 1000-ml volumetric flask, add approximately 500 ml of water, 25 ml of concentrated nitric acid (G4.1) and 75 ml of concentrated hydrochloric acid (G4.2). Add 25.0 ml of intermediate calibration solution B (G4.6.2). Make to 1000 ml with water and mix. This reagent may be stored at room temperature and kept for up to two weeks.

G5 Apparatus

Glassware should be washed using a detergent solution, for example Decon-90 or equivalent and rinsed with water. The glassware should then be soaked in acid solution, for example, 10 % nitric acid, for a minimum of one hour. Glassware should then be rinsed with water, drained, and allowed to dry.

G5.1 Volumetric flasks: 100 ml, 500 ml, 1 litre.

G5.2 Auto-pipettes (variable): 0.1-1 ml, 1-5 ml, 1-10 ml.

G5.3 Continuous flow cold vapour atomic fluorescence mercury analyser with auto-sampler.

G5.4 Auto-sampler vials: 15 ml.

G5.5 Top pan balance capable of weighing to ± 0.01 g.

G5.6 Conical flasks: 100 ml.

G5.7 Air condensers.

G5.8 Dispensers: 2 – 10 ml.

G5.9 Filter funnels.

G5.10 Hardened filter papers (capable of fast flow rates): For example Whatman 541 filter papers, or equivalent.

G5.11 Hot-plate.

G6 Sample preparation

This method has been performance tested using air-dried samples (i.e. air at less than 30 °C passed over the soil) and may not be suitable for samples containing significant amounts of water. The use of an air-dried sample rather than an “as received” sample enables a more homogeneous sub-sample to be taken for analysis. The procedures used to prepare crushed, ground, sieved and/or air-dried samples may, however, adversely affect some metals and metal species present in the original sample prior to analysis. This is particularly the case for mercury, which may be lost in the drying process used to prepare the air-dried sample, even at ambient temperatures. Analysts should, therefore, ascertain whether the procedures used to prepare crushed, ground, sieved and/or air-dried samples affect the resulting determination of metal concentrations. In addition, great care should be taken to ensure that the sub-sample is homogeneous, and representative of the bulk material sampled, especially when smaller quantities are required for repeat analyses where high concentrations are found or suspected.

G7 Analytical procedure

Step	Procedure	Note
G7.1	Weigh out 1.0 g of the prepared soil or contaminated land sample (G6) into a 100-ml glass conical flask. See note a. To the flask and ensuring that the neck of the flask is clean, add 7.0 ml of concentrated nitric acid (G4.1). Fit an air condenser to the flask. Add 21.0 ml of concentrated hydrochloric acid (G4.2) to the flask via the condenser and swirl to mix.	(a) If samples are to be reported on a dry weight basis (at 105 °C) rather than on an air-dried basis, (for example at 30 °C or 40 °C) it will be necessary to carry out a dry solids content determination on a separate portion of the air-dried material. The result should be expressed as percent dried solids.
G7.2	Allow the flask to stand at room temperature for at least 20 minutes until any reaction subsides, see note b. Place the flask on a pre-heated hot-plate at a temperature sufficient to reflux the <i>aqua regia</i> . Observe the contents of the flask for several minutes to ensure that any initial reaction is not too vigorous, see note c.	(b) If a vigorous reaction occurs, add a small amount of water slowly down the air condenser until the reaction subsides. Continue to monitor the reaction and repeat if necessary. (c) If the reaction is vigorous, remove the flask from the hot-plate, add a small amount of water slowly down the air condenser until the reaction subsides and return the flask to the hot-plate. Continue to monitor the reaction and repeat if necessary.

G7.3 Gently reflux the contents of the flask for 180 minutes, then remove the flask from the hot-plate and allow to cool to room temperature. Rinse down the air condenser with 20 ml of water and remove the condenser.

G7.4 Filter the cooled extract solution through a filter paper (G5.10) into a 100-ml volumetric flask. Rinse the conical flask with water and filter the rinsings through the filter paper into the volumetric flask. Make to volume with water.

G7.5 Prepare reagent blanks as required using the procedures described in sections G7.1 - G7.4 using the same batch of reagents used for the samples.

G7.6 Prepare an AQC spiked soil sample using an appropriate soil matrix. Commercially available dried and ground soils may be available. See note d.

G7.7 Following manufacturer's instructions, reduce the calibration standard solutions (G4.6.3 - G4.6.8) blank solutions, sample extract solutions and any AQC solutions with the tin chloride solution (G4.4) and quantify the resulting fluorescence at 254 nm. See notes e and f. Between each determination the instrument wash solution (G4.5) is used to rinse the auto-sampler.

(d) For example, spike 1 g of soil with an appropriate amount of mercury and extract the soil following the procedures described in sections G7.1 - G7.4.

(e) Blank solutions, sample extract solutions and any AQC solutions are diluted by a factor of three with water prior to measurement to matrix-match these solutions to the calibration solution.

(f) For sample solutions giving a result outside of the calibration range, the extract solution (G7.4) should be diluted accordingly or consideration given to repeating the analysis using a smaller quantity of sample (G7.1) or using more *aqua regia* and making to a larger volume (G7.4).

G8 Calculations

The concentration of the element in the sample is given by:

$$C_{\text{sample}} = (C_{\text{extract}} \times V_{\text{extract}} \times \text{DF}) / M_{\text{sample}}$$

Where C_{sample} is the concentration of the element in the air-dried sample (mg/kg); C_{extract} is the concentration of element in the sample extract solution (mg/l); V_{extract} is the volume of extract (ml, usually 100 ml, section G7.4); DF is the dilution factor, if any (note f, section G7.7); and M_{sample} is the mass of sample (g, usually 1 g, section G7.1).

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed. In addition, the reporting of results may also need to take into account whether results are calculated on an air-dried basis (for example at 30 °C) or on a dry weight basis (at 105 °C).

When an air-dried sample is prepared, and from this say A % of inert extraneous material is removed, then if (excluding inert extraneous material)

moisture content on air-dried matter = B %
 and
 metal concentration on air-dried matter = C mg/kg
 then
 metal concentration on dry weight basis = $(C \times 100) / (100 - B)$ mg/kg

If the inert extraneous material needs to be taken into account, then

metal concentration on air-dried matter = $(C \times (100-A))/100$ mg/kg
 and
 metal concentration on dry weight basis = $((C \times 100)/(100-B)) \times ((100 - ((A \times 100)/(100-B)))/100)$ mg/kg

Table G1 Performance data for mercury

Certified Reference Material	CRM value (mg/kg)	Bias (%)	RSD (%)
7002	0.080	12.6	11.9
7003	0.093	-12.8	15.9
7004	0.21	-2.9	5.5
2711	6.25	-2.6	3.3
Spiked soil	Mean value (mg/kg)	Bias (%)	RSD (%)
sandy/loam + 1.5 mg/kg	1.496	-4.2	4.8
sandy/loam + 5.0 mg/kg	5.076	0.4	4.7

Performance data provided by Analytical and Environmental Services Ltd.

LOD (of 0.06 mg/kg) is calculated as 5 x within batch standard deviation of blank soil extracts (acid washed quartz) following analysis of 11 batches in duplicate.

CRM 7002 is a dried homogenised sieved sand soil to less than 100 µm.
 CRM 7003 is a dried homogenised sieved clay soil to less than 100 µm.
 CRM 7004 is a dried homogenised sieved loam soil to less than 100 µm.
 CRM NIST 2711 is a dried homogenised sieved moderately contaminated agricultural soil to less than 74 µm.

Results with a high bias may indicate that the CRM value may need to be checked (for example total or extractable value and methodology used to generate the reference value) or that the procedure used for that element may be inappropriate for the determination of that element in the matrix.

H The determination of selected trace elements in sediments, soils and solid waste samples by *aqua regia* extraction using inductively coupled plasma-optical emission spectrometry

H1 Performance characteristics of method

H1.1	Substance determined	Arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, molybdenum, nickel, selenium, thallium vanadium, and zinc.
H1.2	Type of sample	Sediment, soil, contaminated land and other solid waste samples.
H1.3	Basis of method	Trace metals in sediments, soils, contaminated land or solid waste samples are extracted with <i>aqua regia</i> and diluted with water. The metal concentrations in the resulting solution are determined using ICP-OES.
H1.4	Range of application	Up to 500 mg/kg for arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, molybdenum, nickel, selenium, thallium, vanadium. Up to 100 mg/kg for mercury. Up to 1000 mg/kg for zinc. Up to 2500 mg/kg for manganese and barium. Calibration ranges may be extended by appropriate dilution of the <i>aqua regia</i> extract solution.
H1.5	Performance data	See Table H1.
H1.6	Interferences	Chemical: These are mostly eliminated by the high temperature in the plasma. For samples containing high concentrations (i.e. >1000 mg/kg) of easily ionised elements, a suppression or enhancement of emission signal can occur. Spectral: Most ICP-OES interferences are spectral in origin. The ICP is an efficient excitation source, causing almost all elements to emit at numerous wavelengths. The analytical wavelength should be selected to avoid spectral overlap from other elements known to be present in the sample matrix. Background: Suitable background correction should be selected by inspection of spectra for typical blanks, standards and samples.

H2 Principle

Metals are extracted from dried, ground sediments, soils, contaminated land and other solid waste samples by the addition of *aqua regia*, followed by heating using a digestion block. The extract is cooled and made to volume with water. The concentration of the extracted metal is determined by ICP-OES against calibration solutions prepared in *aqua regia*.

H3 Hazards

Appropriate personal protective equipment should be worn when handling reagents and potentially contaminated or hazardous samples. Concentrated acids should always be added to water and the operation carried out in a fume cupboard. The extract solutions contain concentrated acids and should be handled with care.

H4 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interference in the analysis. These should be checked for each batch of chemicals and reagents and verified by running reagent blanks with each batch of samples analysed. Reagents should be stored in sealed containers or other suitable vessels, stored at room temperature and kept in the dark, if necessary.

Water should be deionised (specific conductivity of less than 10 $\mu\text{S}/\text{cm}$) and volumetric glassware should be of at least grade B quality (preferably grade A). All reagents should be appropriately labelled, including the expiry date of the reagent. The preparation of these reagents should be recorded.

H4.1 Concentrated nitric acid (SG 1.42).

H4.2 Concentrated hydrochloric acid (SG 1.18).

H4.3 Nitric acid (10 %). This solution is used for diluting extracts and for cleaning glassware. Add 4000 ml of water to a 5 litre volumetric flask, add 500 ml of concentrated nitric acid (H4.1). Mix well, allow the solution to cool and make up to 5000 ml with water. The solution may be stored at room temperature for up to a month.

H4.4 Mixed stock calibration solution. A mixed stock calibration solution containing arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, molybdenum, nickel, selenium, thallium, vanadium and zinc, each at a concentration of 100 mg/l is usually available commercially and may be stored at room temperature for up to 12 months.

H4.5 Separate stock solutions containing 1000 mg/l barium, mercury, manganese and zinc are usually available commercially and may be stored at room temperature for up to 12 months.

H4.6 Working calibration blank solution. To a 200-ml volumetric flask containing 100 ml of water, add 5.0 ml of concentrated nitric acid (H4.1) and 15.0 ml of concentrated hydrochloric acid (H4.2). Make to volume with water and mix well. This solution may be stored in a high density plastic bottle at room temperature for up to 3 months.

H4.7 Working calibration solution (5 mg/l). To a 200-ml volumetric flask containing 100 ml of water, add 5.0 ml of concentrated nitric acid (H4.1) and 15.0 ml of concentrated hydrochloric acid (H4.2). Mix well, and add 10.0 ml of mixed stock calibration solution (H4.4). Make to volume with water and mix well. This solution may be stored in a high density plastic bottle at room temperature for up to 3 months.

H4.8 Working calibration solution (10 mg/l). To a 200-ml volumetric flask containing 100 ml of water, add 5.0 ml of concentrated nitric acid (H4.1) and 15.0 ml of concentrated hydrochloric acid (H4.2). Mix well, and add 20.0 ml of mixed stock calibration solution (H4.4). Make to volume with water and mix well. This solution may be stored in a high density plastic bottle at room temperature for up to 3 months.

H4.9 Working calibration solution (50 mg/l manganese and 20 mg/l zinc). To a 200-ml volumetric flask containing 100 ml of water, add 5.0 ml of concentrated nitric acid (H4.1) and 15.0 ml of concentrated hydrochloric acid (H4.2) mix well and add 10.0 ml of the manganese stock solution (H4.5) and 4.0 ml of the zinc stock solution (H4.5). Make to volume with water and mix well. This solution may be stored in a high density plastic bottle at room temperature for up to 3 months.

H4.10 Working calibration solution (25 mg/l barium and 0.5 mg/l mercury). To a 200-ml volumetric flask containing 100 ml of water, add 5.0 ml of concentrated nitric acid (H4.1) and 15.0 ml of concentrated hydrochloric acid (H4.2). Mix well and add 5.0 ml of the barium stock solution (H4.5) and 0.1 ml of the mercury stock solution (H4.5). Make to volume with water and mix well. This solution may be stored in a high density plastic bottle at room temperature for up to 3 months.

H4.11 Working calibration solution (50 mg/l barium and 1.0 mg/l mercury). To a 200-ml volumetric flask containing 100 ml of water, add 5.0 ml of concentrated nitric acid (H4.1) and 15.0 ml of concentrated hydrochloric acid (H4.2). Mix well and add 10.0 ml of the barium stock solution (H4.5) and 0.2 ml of the mercury stock solution (H4.5). Make to volume with water and mix well. This solution may be stored in a high density plastic bottle at room temperature for up to 3 months.

H4.12 AQC soil. A laboratory reference material comprising a spiked soil is used for AQC purposes for *aqua regia* extracted samples.

H4.13 Independent AQC solutions. These solutions are of the same concentrations as the calibration solutions described in sections H4.7 and H4.11. These solutions provide, if required, an independent check of the calibration prior to sample analysis.

H5 Apparatus

Cleanliness is an essential requirement for all extractions of trace metals from sediment, soil, contaminated land and other solid waste samples. Glassware should be washed using a detergent solution, for example Decon 90, and rinsed with water. The glassware should then be soaked in dilute nitric acid solution (H4.3) for at least 24 hours before use and rinsed thoroughly with water.

H5.1 Top pan balance capable of weighing to ± 0.01 g.

H5.2 250 ml glass digestion tubes with associated glass reflux condensers or 50 ml plastic digestion tubes with associated glass cold finger condensers.

- H5.3 Thermostatically controlled temperature digestion block capable of maintaining a temperature of 160 °C.
- H5.4 Thermostatically controlled temperature digestion block capable of maintaining a temperature of 120 °C.
- H5.5 Volumetric flasks (grade B or better)
- H5.6 Dispensers - 0.1 ml to 20 ml capacity.
- H5.7 Centrifuge, syringes, 0.45 µm cartridge filters.
- H5.8 ICP optical emission spectrometer equipped with auto-sampler and with instrument control and data handling system.
- H5.9 Auto-sampler plastic tubes and pump tubes.
- H5.10 Gases: argon >99.99 %, nitrogen >99.99 %.

H6 Sample preparation

Sediment, soil, contaminated land and other solid waste samples should be air-dried at less than 30 °C. The loss on drying should be recorded. For example, spread a portion of sample onto a tray and place the tray in an oven (set at less than 30 °C) until dry, for example overnight or for a longer time if necessary. Using a plastic spatula, gently break up any lumps. Any large rocks, bricks and other inert material greater than 10 mm should be hand picked and removed. Record the total weight of any discarded material. The sample should then be sieved through a 10 mm sieve. (Soil being assessed for disposal to land for agricultural purposes need not undergo sieving through the 10 mm sieve but should be sieved through a 2 mm sieve). The sieved sample should then be jaw-crushed, if required, and ball-milled using agate pots and balls to obtain a homogeneous fraction for subsequent extraction and analysis. (If the material is very hard then a tungsten carbide milling system should be used). The prepared sample should be stored in an air-tight plastic container.

H7 Analytical procedure

Step	Procedure	Note
H7.1 250 ml Glass Tube Sample Digestion		
H7.1.1	Weigh out 1.0 g of the prepared air-dried and ground sample (H6) into an anti-static weighing boat. Transfer the sample to a 250 ml glass digestion tube and reweigh the weighing boat, record the weight of sample. See note a.	(a) An AQC soil sample and blank sample should be similarly weighed and treated.
H7.1.2	Place the tube in a fume-extracted area and carefully add 2.5 ml of concentrated nitric acid (H4.1) followed by 7.5 ml of concentrated hydrochloric acid (H4.2). See note b. Cover the tube loosely, for example with	(b) Care should be taken, as samples that contain a high carbonate content will effervesce.

polyethylene film material and allow the sample to stand at room temperature in a fume-extracted area for a minimum of eight hours, see note c.

H7.1.3 Switch on the heating block and reflux condenser re-circulating water bath. Place the tube into the heating block and connect the reflux water condenser. Start the heating block digestion program, see note d. After heating, allow the solution to cool.

H7.1.4 Rinse down the inside of the condenser with a small portion of water, and allow the water to drain into the digestion tube. Quantitatively transfer the contents of the digestion tube into a 50 ml plastic centrifuge tube. Rinse the digestion tube with water and transfer the rinsings to the centrifuge tube. Make to 50 ml with water, mix well and then allow sample to stand, see note e.

H7.2 50 ml Plastic Tube Sample Digestion

H7.2.1 Weigh out 1.0 g of the prepared air-dried and ground sample (H6) into an anti-static weighing boat. Transfer the sample to a 50 ml plastic digestion tube and reweigh the weighing boat, record the weight of sample. See note a.

H7.2.2 Place the tube in a fume-extracted area and carefully add 2.5 ml of concentrated nitric acid (H4.1) followed by 7.5 ml of concentrated hydrochloric acid (H4.2). See note b. Cover the tube loosely with a lid. Allow the sample to stand at room temperature in a fume-extracted area for a minimum of eight hours, see note c.

H7.2.3 Place the tube in the digestion block, remove the lid and place a glass cold-finger condenser over the tube. Switch on the heating block and start the heating block digestion program, see note f. After heating, allow the solution to cool.

H7.2.4 Rinse down the condenser with a small portion of water, and allow the water to drain into the digestion tube. Make to 50 ml with water, place a lid on the tube, mix well and then

(c) The sample may be left overnight at this stage.

(d) For example the following programme has been found suitable:
60 °C for 10 minutes,
80 °C for 10 minutes,
100 °C for 10 minutes,
160 °C for 2 hours, and finally,
30 minutes cooling time.

(e) On standing, most samples will settle to give a clear solution. If not, centrifuge the suspension or filter using a syringe and 0.45 µm filter cartridge.

(f) For example the following programme has been found suitable:
linear temperature ramp from room temperature to 120 °C in 50 minutes,
hold at 120 °C for 150 minutes, and finally, allow to cool.

allow sample to stand, see note e.

H7.3 ICP-OES determination

H7.3.1 Following manufacturer's instructions set up the ICP-OES instrument using the wavelengths listed in Table H2.

H7.3.2 Perform system suitability checks to verify instrument performance.

H7.3.3 Calibrate the instrument using the calibration solutions (H4.6 to H4.11) see note g.

(g) If required, the calibration may be checked, by running the AQC solutions described in section H4.13, prior to sample analysis.

H7.3.4 Analyse the sample blank, AQC sample and sample extracts at the appropriate frequency. Between each sample the sample introduction system should be rinsed using the dilute nitric acid (H4.3). See notes h and i.

(h) The instrument may be re-calibrated as required to maintain performance.

(i) For samples with concentrations exceeding the calibration range, the extract solution (H7.1.4, H7.2.4) should be appropriately diluted with dilute nitric acid (H4.3) and re-analysed. Alternatively, repeat the extraction with a smaller quantity of sample (H7.1.1, H7.2.1) or use more *aqua regia* and make to a larger volume (H7.1.4, H7.2.4) if appropriate.

H8 Calculations

The concentration of the element in the sample is given by:

$$C_{\text{sample}} = (C_{\text{extract}} \times V_{\text{extract}} \times DF) / M_{\text{sample}}$$

Where C_{sample} is the concentration of the element in the air-dried sample (mg/kg);
 C_{extract} is the concentration of element in the sample extract solution (mg/l);
 V_{extract} is the volume of extract (ml, usually 50 ml, sections H7.1.4 and H7.2.4);
DF is the dilution factor, if any (note i, section H7.3.4); and
 M_{sample} is the mass of sample (g, usually 1 g, sections H7.1.1 and H7.2.1).

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed. In addition, the reporting of results may also need to take into account whether results are calculated on an air-dried basis (for example at 30 °C) or on a dry weight basis (at 105 °C).

When an air-dried sample is prepared, and from this say A % of inert extraneous material is removed, then if (excluding inert extraneous material)

moisture content on air-dried matter = B %

and

metal concentration on air-dried matter = C mg/kg

then

metal concentration on dry weight basis = $(C \times 100) / (100 - B)$ mg/kg

If the inert extraneous material needs to be taken into account, then

metal concentration on air-dried matter = $(C \times (100 - A)) / 100$ mg/kg

and

metal concentration on dry weight basis = $((C \times 100) / (100 - B)) \times ((100 - ((A \times 100) / (100 - B))) / 100)$ mg/kg

Table H1 Performance data

Table H1.1 250 ml Glass Tube Digestion Method

Element	Certified Reference Material								
	LGC 6135 (ERM-CC135a)			LGC 6138			LGC 6144		
	CRM value (mg/kg)	Bias (%)	RSD (%)	CRM value (mg/kg)	Bias (%)	RSD (%)	CRM value (mg/kg)	Bias (%)	RSD (%)
arsenic	66.0	-3.1	1.9	34.5	3.8	3.4	14.9	5.9	4.7
barium	134	5.2	2.5						
cobalt	20.0	-5.5	2.7						
chromium	336	6.4	1.8	99.3	5.3	1.9	118	3.5	2.7
copper	105	-0.4	3.1	132	-0.8	5.9	71.0	-2.0	6.8
manganese	348	6.9	1.7						
nickel	277	1.7	2.6	33.5	3.7	15.0	27.0	10.6	10.1
lead	391	-0.7	1.5	490	0.8	4.2	196	0.0	3.9
vanadium	78.0	10.1	2.2	54.6	5.1	1.4	38.0	-3.7	3.0
zinc	316	4.0	1.7	456	7.2	2.4	192	10.5	2.9

Table H1.2 250 ml Glass Tube Digestion Method

Element	Certified Reference Material					
	LGC 6137			LGC 6139		
	CRM value (mg/kg)	Bias (%)	RSD (%)	CRM value (mg/kg)	Bias (%)	RSD (%)
arsenic	12.4	5.1	7.2	27.0	3.7	3.1
barium	82.0	3.6	5.0			
cadmium				2.3	-4.2	5.1
cobalt	13.7	-9.9	3.5			
chromium	47.0	-9.7	4.1	80.0	-3.8	2.8
copper	31.6	-5.5	4.7	92.0	-5.5	2.0
manganese	665	-3.6	3.6			
nickel	31.5	-4.7	3.8	38.0	-4.9	3.0
lead	73.0	-3.4	4.4	160	-5.0	2.7
vanadium	47.0	-9.4	2.8			
zinc	231	-3.4	3.2	513	-7.2	2.2

Table H1.3 50 ml Plastic Tube Digestion Method

Element	LOD (mg/kg)	Certified Reference Material								
		RTC-CRM037-050			RTC-CRM048-050			RTC-CRM 052-050		
		CRM value (mg/kg)	Bias (%)	RSD (%)	CRM value (mg/kg)	Bias (%)	RSD (%)	CRM value (mg/kg)	Bias (%)	RSD (%)
arsenic	2	73	-5.6	3.4	150	2.0	3.2	14.6	3.8	7.7
barium	5	354	1.9	6.1	149	6.8	3.0	137	-2.3	4.8
beryllium	0.1	99.2	-3.4	3.1	64.9	-0.7	3.2	26.1	-1.2	4.7
cadmium	0.2	91.7	-1.9	3.5	159	1.0	3.2	35.6	-1.2	4.1
cobalt	1	72.1	-2.2	3.2	74.1	2.4	3.4	26.3	-0.3	4.7
chromium	2	118	0.1	3.5	113	4.5	3.4	30.7	-5.4	4.9
copper	1	129	-1.3	3.7	144	-1.7	3.3	44.2	-3.1	4.3
mercury	1	30.7	-14.0	6.2	13.5	-13.5	4.1	0.815*	-26.4	35.6
manganese	1	560	8.2	3.3	565	15.2	2.8	187	0.1	5.0
molybdenum	1	76.5	1.5	3.7	76.2	1.4	3.4	38.9	-4.0	4.2
nickel	1	289	-6.4	3.4	166	-1.8	3.2	28.6	-3.1	4.5
lead	5	118	-2.2	3.3	100	2.6	3.0	82.6	0.7	4.5
selenium	3	145	-3.9	3.1	137	2.7	3.4	8.24	15.1	19.7
thallium	3	154	-5.6	3.6	109	-1.9	3.4			
vanadium	1	86.9	11.9	3.3	120	7.2	3.2	88.4	-4.1	4.7
zinc	5	403	6.3	3.6	332	10.2	2.8	89	5.4	4.2

Performance data provided by Environment Agency's National Laboratory Service

* value below method LOD

LOD is calculated as $2t_{0.05}\sqrt{2}$ times the within batch standard deviation of a blank clean sand (RTC-CLNSAND4) following analysis of 11 batches in duplicate.

LGC 6135 (ERM-CC135a) is a dried ground sieved (<100 µm) homogenised contaminated brick works soil.

LGC 6138 is a dried ground sieved (<200 µm) homogenised coal-carbonisation site soil.

LGC 6144 is a dried ground sieved (<200 µm) homogenised gas works contaminated soil.

LGC 6137 is a dried ground sieved (<200 µm) homogenised estuarine sediment.

LGC 6139 is a dried ground sieved (<500 µm) homogenised river clay sediment.

RTC CRM 037-050 is a dried sieved and homogenised sandy loam.

RTC CRM 048-050 is a dried sieved and homogenised sand.

RTC CRM 052-050 is a dried sieved and homogenised loamy clay.

Results with a high bias may indicate that the CRM value may need to be checked (for example total or extractable value and methodology used to generate the reference value) or that the procedure used for that element may be inappropriate for the determination of that element in the matrix.

Table H2 ICP-OES wavelengths

Element	Wavelength (nm)
arsenic	188.979
barium	233.527
beryllium	313.107
cadmium	228.802
cobalt	228.616
chromium	267.716
copper	324.754
mercury	194.168
manganese	257.610
molybdenum	202.030
nickel	232.003
lead	220.353
selenium	196.026
thallium	190.801
vanadium	292.402
zinc	213.856

All wavelengths are axially orientated.

An inter-element correction is applied for chromium on nickel.

I The determination of mercury in soils and solid waste samples by *aqua regia* extraction using cold vapour atomic fluorescence spectrometry

I1 Performance characteristics of method

I1.1	Substance determined	Mercury.
I1.2	Type of sample	Soil, contaminated land and other solid waste samples.
I1.3	Basis of method	Mercury in soils, contaminated land or solid waste samples are extracted with <i>aqua regia</i> and diluted with water. The mercury concentration in the resulting solution is determined using cold vapour atomic fluorescence spectrometry.
I1.4	Range of application	Up to 1 mg/kg for mercury. The calibration range may be extended by taking a smaller aliquot of the <i>aqua regia</i> extract solution or diluting the <i>aqua regia</i> extract solution.
I1.5	Performance data	See Table I1.
I1.6	Interferences	No significant interferences.

I2 Principle

Metals are extracted from dried, ground soils, contaminated land and other solid waste samples by the addition of *aqua regia*, followed by heating using a digestion block. The extract is cooled and made to volume with water. The extracted mercury (i.e. Hg^{2+}) is reduced to mercury vapour with acidic stannous chloride solution. Mercury is quantified by removal of the vapour from the solution, by a stream of argon and carried to a cell illuminated by a mercury lamp with a fluorescence detector at a wavelength of 254 nm.

I3 Hazards

Appropriate personal protective equipment should be worn when handling reagents and potentially contaminated or hazardous samples. Concentrated acids should always be added to water and the operation carried out in a fume cupboard. The extract solutions contain concentrated acids and should be handled with care.

I4 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interference in the analysis. Hydroxylammonium chloride should be of a quality "low in mercury". These should be checked for each batch of chemicals and reagents and verified by running reagent blanks with each batch of samples analysed. Reagents should be stored in sealed containers or other suitable vessels, stored at room temperature and kept in the dark, if necessary.

Water should be deionised (specific conductivity of less than 10 $\mu\text{S}/\text{cm}$) and volumetric glassware should be of at least grade B quality (preferably grade A). All reagents should be appropriately labelled, including the expiry date of the reagent. The preparation of these reagents should be recorded.

14.1 Concentrated nitric acid (SG 1.42).

14.2 Concentrated hydrochloric acid (SG 1.18).

14.3 Tin(II) chloride solution (2 % w/v). To a 100-ml measuring cylinder, in a fume cupboard, add 40 ml of concentrated hydrochloric acid (14.2) and 10.0 g of stannous chloride (SnCl_2) and stir to dissolve the reagent. Carefully transfer the contents to a 500-ml measuring cylinder containing 250 ml of water. Make to the 500-ml mark with water and mix well. To remove any mercury contamination, bubble argon through the solution for at least 30 minutes at the rate of 1 litre per minute. Store in a glass or high density plastic bottle. This solution should be prepared on the day of use.

14.4 Potassium dichromate and nitric acid fixing solution. To a 1000-ml measuring cylinder, add 250 ml of water and 12.5 g of potassium dichromate, and stir to dissolve the reagents. Transfer the cylinder to a fume cupboard, carefully add 250 ml of concentrated nitric acid (14.1) allow the solution to cool and store in a glass or high density plastic bottle. This solution may be stored at room temperature for up to six months.

14.5 Potassium bromide/bromate solution. To a 1000-ml measuring cylinder, add 250 ml of water and 10.0 g of potassium bromide and 2.8 g of potassium bromate, and stir to dissolve the reagents. Make to the 1000-ml mark with water, mix well and store in a glass or high density plastic bottle. This solution may be stored at room temperature for up to six months.

14.6 Hydroxylammonium chloride solution. To a 500-ml measuring cylinder, add 200 ml of water and 9.6 g of hydroxylammonium chloride, and stir to dissolve the reagent. Make to the 400-ml mark with water, mix well and store in a glass or high density plastic bottle. This solution may be stored at room temperature for up to six months.

14.7 Calibration stock solution (1000 mg/l). Stock solution containing 1000 mg/l of mercury is usually available commercially and may be stored at room temperature for up to twelve months.

14.8 Intermediate calibration stock solution 1 (10 mg/l). To a 100-ml volumetric flask containing 50 ml of water, add 2.0 ml of potassium dichromate and nitric acid fixing solution (14.4) and 1.0 ml of calibration stock solution (14.7). Make to volume with water and mix well. This solution may be stored at room temperature for up to six months.

14.9 Intermediate calibration stock solution 2 (1000 $\mu\text{g}/\text{l}$). To a 50-ml volumetric flask containing 25 ml of water, add 1.0 ml of potassium dichromate and nitric acid fixing solution (14.4) and 5.0 ml of intermediate calibration stock solution 1 (14.8). Make to volume with water and mix well. This solution may be stored at room temperature for up to three months.

- 14.10 Intermediate calibration stock solution 3 (10 µg/l). To a 500-ml volumetric flask containing 200 ml of water, add 10 ml of potassium dichromate and nitric acid fixing solution (14.4) and 5.0 ml of intermediate calibration stock solution 2 (14.9). Make to volume with water and mix well. This solution may be stored at room temperature for up to three months.
- 14.11 Calibration blank solution. To a 200-ml volumetric flask containing 100 ml of water, add 4.0 ml of potassium dichromate and nitric acid fixing solution (14.4). Make to volume with water and mix well. This solution may be stored at room temperature for up to one week.
- 14.12 Calibration solution 1 (0.25 µg/l). To a 200-ml volumetric flask containing 100 ml of water, add 4.0 ml of potassium dichromate and nitric fixing acid solution (14.4) and 5.0 ml of intermediate calibration stock solution 3 (14.10). Make to volume with water and mix well. This solution may be stored at room temperature for up to one week.
- 14.13 Calibration solution 2 (0.50 µg/l). To a 200-ml volumetric flask containing 100 ml of water, add 4.0 ml of potassium dichromate and nitric acid fixing solution (14.4) and 10.0 ml of intermediate calibration stock solution 3 (14.10). Make to the mark with water and mix well. This solution may be stored at room temperature for up to one week.
- 14.14 Independent AQC solutions. These solutions provide an independent check of the calibration.
- 14.15 AQC stock solution A (1000 mg/l). Stock solution containing 1000 mg/l of mercury is usually available commercially and may be stored at room temperature for up to twelve months.
- 14.16 AQC stock solution B (10 mg/l). To a 100-ml volumetric flask containing 50 ml of water, add 5.0 ml of concentrated nitric acid (14.1) and 1.0 ml of AQC stock solution A (14.15). Make to volume with water and mix well. This solution may be stored at room temperature for up to six months.
- 14.17 AQC stock solution C (500 µg/l). To a 100-ml volumetric flask containing 50 ml of water, add 1.0 ml of concentrated nitric acid (14.1) and 5.0 ml of AQC mercury stock solution B (14.16). Make to volume with water and mix well. This solution may be stored at room temperature for up to one month.
- 14.18 AQC stock solution D (10 µg/l). To a 100-ml volumetric flask containing 50 ml of water, add 1.0 ml of concentrated nitric acid (4.1) and 2.0 ml of AQC mercury stock solution C (14.17). Make to volume with water and mix well. This solution may be stored at room temperature for up to one month.
- 14.19 Working AQC solution (0.1 µg/l). To a 1000-ml volumetric flask containing 200 ml of water, add 20.0 ml of potassium dichromate and nitric acid fixing solution (14.4) and 10.0 ml of AQC stock solution D (14.18). Make to the mark with water and mix well. This solution may be stored at room temperature for up to one month.

14.20 AQC blank solution. To a 1000-ml volumetric flask containing 200 ml of water, add 20.0 ml of potassium dichromate and nitric acid fixing solution (14.4). Make to the mark with water and mix well. This solution may be stored at room temperature for up to one month.

14.21 AQC soil. A laboratory reference material comprising a spiked soil should be used for AQC purposes for *aqua regia* extracted samples.

14.22 Instrument set-up solution. To a 1000-ml volumetric flask containing 200 ml of water, add 20.0 ml of potassium dichromate and nitric acid fixing solution (14.4) and 50 ml of intermediate calibration stock solution 3 (14.10). Make to the mark with water and mix well. This solution may be stored at room temperature for up to one month.

14.23 Dilution solution. To a 500-ml volumetric flask containing 100 ml of water, add 10.0 ml of potassium dichromate and nitric acid fixing solution (14.4). Make to the mark with water and mix well. This solution may be stored at room temperature for up to one month.

15 Apparatus

Cleanliness is an essential requirement for all extractions of trace metals from soil, contaminated land and other solid waste samples. Glassware should be washed using a detergent solution, for example Decon 90, and rinsed with water. The glassware should then be soaked in dilute nitric acid solution (14.3) for at least 24 hours before use and rinsed thoroughly with water.

15.1 Top pan balance capable of weighing to ± 0.01 g.

15.2 250 ml glass digestion tubes with associated glass reflux condensers or 50 ml plastic digestion tubes with associated glass cold finger condensers.

15.3 Thermostatically controlled temperature digestion block capable of maintaining a temperature of 160 °C.

15.4 Thermostatically controlled temperature digestion block capable of maintaining a temperature of 120 °C.

15.5 Volumetric flasks (grade B or better) - 50-ml, 100-ml, 200-ml, 500-ml, 1000-ml capacity.

15.6 Measuring cylinders - 100-ml, 500-ml, 1000-ml capacity.

15.7 Dispensers - 0.1 ml to 20 ml capacity.

15.8 Centrifuge, syringes, 0.45 μ m cartridge filters.

15.9 Reduction equipment, mercury lamp, fluorescence detection system with auto-sampler and with instrument control and data handling system.

15.10 Auto-sampler plastic cups (27 ml) and pump tubes.

I5.11 Gases: Argon >99.99 %.

I6 Sample preparation

Soil, contaminated land and other solid waste samples should be air-dried at less than 30 °C. The loss on drying should be recorded. For example, spread a portion of sample onto a tray and place the tray in an oven (set at less than 30 °C) until dry, for example overnight or for a longer time if necessary. Using a plastic spatula, gently break up any lumps. Any large rocks, bricks and other inert material greater than 10 mm should be hand picked and removed. Record the total weight of any discarded material. The sample should then be sieved through a 10 mm sieve. (Soil being assessed for disposal to land for agricultural purposes need not undergo sieving through the 10 mm sieve but should be sieved through a 2 mm sieve). The sieved sample should then be jaw-crushed, if required, and ball-milled using agate pots and balls to obtain a homogeneous fraction for subsequent extraction and analysis. (If the material is very hard then a tungsten carbide milling system should be used). The prepared sample should be stored in an air-tight plastic container.

I7 Analytical procedure

Step	Procedure	Note
17.1	250 ml Glass Tube Sample Digestion	
17.1.1	Weigh out 1.0 g of the prepared air-dried and ground sample (I6) into an anti-static weighing boat. Transfer the sample to a 250 ml glass digestion tube and reweigh the weighing boat, record the weight of sample, see note a.	(a) An AQC soil sample and blank sample should be similarly weighed.
17.1.2	Place the tube in a fume-extracted area and carefully add 2.5 ml of concentrated nitric acid (I4.1) followed by 7.5 ml of concentrated hydrochloric acid (I4.2), see note b. Cover the tube loosely, for example with polyethylene film material and allow the sample to stand at room temperature in a fume-extracted area for a minimum of eight hours, see note c.	(b) Care should be taken, as samples that contain a high carbonate content will effervesce. (c) The sample may be left overnight at this stage.
17.1.3	Switch on the heating block and reflux condenser re-circulating water bath. Place the tube into the heating block and connect the reflux water condenser. Start the heating block digestion program, see note d. After heating, allow the solution to cool.	(d) For example the following programme has been found suitable: 60 °C for 10 minutes, 80 °C for 10 minutes, 100 °C for 10 minutes, 160 °C for 2 hours, and finally, 30 minutes cooling time.
17.1.4	Rinse down the inside of the condenser with a small portion of water, and allow the	(e) On standing, most samples will settle to give a clear solution. If not,

water to drain into the digestion tube. Quantitatively transfer the contents of the digestion tube into a 50 ml plastic centrifuge tube. Rinse the digestion tube with water and transfer the rinsings to the centrifuge tube. Make to 50 ml with water, mix well and then allow sample to stand, see note e.

centrifuge the suspension or filter using a syringe and 0.45 µm filter cartridge.

17.2 50 ml Plastic Tube Sample Digestion

17.2.1 Weigh out 1.0 g of the prepared air-dried and ground sample (I6) into an anti-static weighing boat. Transfer the sample to a 50 ml plastic digestion tube and reweigh the weighing boat, record the weight of sample. See note a.

17.2.2 Place the tube in a fume-extracted area and carefully add 2.5 ml of concentrated nitric acid (I4.1) followed by 7.5 ml of concentrated hydrochloric acid (I4.2). See note b. Cover the tube loosely with a lid. Allow the sample to stand at room temperature in a fume-extracted area for a minimum of eight hours, see note c.

17.2.3 Place the tube in the digestion block, remove the lid and place a glass cold-finger condenser over the tube. Switch on the heating block and start the heating block digestion program, see note f. After heating, allow the solution to cool.

(f) For example the following programme has been found suitable: linear temperature ramp from room temperature to 120 °C in 50 minutes, hold at 120 °C for 150 minutes, and finally, allow to cool.

17.2.4 Rinse down the condenser with a small portion of water, and allow the water to drain into the digestion tube. Make to 50 ml with water, place a lid on the tube, mix well and then allow sample to stand, see note e.

17.3 Hg²⁺ oxidation state generation

17.3.1 Dispense 0.20 ml of extract solution (I7.1.4 or I7.2.4) into a plastic auto-sampler cup and add 9.8 ml of dilution solution (I4.23) see note g.

(g) Whatever aliquot volume is taken, this should, where appropriate, be made to 10.0 ml with dilution solution (I4.23).

Dispense 2.0 ml of blank extract solution into a plastic auto-sampler cup and add 8.0 ml of dilution solution (I4.23).

Dispense 0.20 ml of AQC solution (I4.19) into a plastic auto-sampler cup and add 9.8 ml of dilution solution (I4.23).

Dispense 10.0 ml of the calibration solutions (I4.11- I4.13) into separate plastic auto-sampler cups.

To each auto-sampler cup, add 1.0 ml of concentrated hydrochloric acid (I4.2) and then 0.25 ml of potassium bromide/bromate solution (I4.5) and allow the solution to stand for at least 30 minutes.

17.3.2 Add to the cup 0.5 ml of hydroxyammonium chloride solution (I4.6) and allow the solution to stand for a further 30 minutes. See note h.

(h) This reagent decolourises the potassium dichromate.

17.4 Instrument set-up solution

17.4.1 Dispense 60 ml of instrument set-up solution (I4.22) into a 100 ml plastic pot, add 6.0 ml of concentrated hydrochloric acid (I4.2) and 1.5 ml of potassium bromide/bromate solution (I4.5) and leave for at least 30minutes.

17.4.2 Add to the cup 3.0 ml of hydroxyammonium chloride solution (I4.6) and allow to stand for a further 30 minutes.

17.5 Cold vapour atomic fluorescence mercury determination

17.5.1 Following the manufacturer's instructions set up the cold vapour atomic fluorescence instrument. See note i.

(i) Ensure the stannous chloride solution (I4.3) and water wash reservoirs are full and the argon flow is set correctly.

17.5.2 Perform instrument check using set-up solution (17.4) and system suitability checks to verify instrument performance.

17.5.3 Calibrate the instrument using the calibration solutions (I7.3) see note j.

(j) If required, the calibration may be checked, by running the AQC solutions (I4.19) prior to sample analysis.

17.5.4 Analyse the blank, AQC solution, sample blank, AQC soil and sample extracts (I7.3) at the appropriate frequency. Between each sample the system should be set to rinse using the water. See notes k and l.

(k) The instrument may be re-calibrated as required to maintain performance.

(l) For samples with concentrations exceeding the calibration range, the extract solution (I7.1.4, I7.2.4) should be appropriately diluted with dilution

solution (I4.23) or a smaller aliquot (I7.3.1) taken and the analysis repeated. Alternatively, repeat the extraction with a smaller quantity of sample (I7.1.1, I7.2.1) or use more *aqua regia* and make to a larger volume (I7.1.4, I7.2.4) if appropriate.

I8 Calculations

The concentration of the element in the sample is given by:

$$C_{\text{sample}} = (C_{\text{extract}} \times V_{\text{extract}} \times V_{\text{oxidation}} \times \text{DF}) / M_{\text{sample}} \times V_{\text{aliquot}}$$

Where C_{sample} is the concentration of the element in the air-dried sample (mg/kg);
 C_{extract} is the concentration of element in the sample extract solution (mg/l);
 V_{extract} is the volume of extract (ml, usually 50 ml, section I7.1.4, I7.2.4);
 $V_{\text{oxidation}}$ is the oxidation volume (section I7.3.1, usually 10 ml);
 V_{aliquot} is the aliquot volume of extract (note g of I7.3.1);
DF is the dilution factor, if any (note I, section I7.5.4); and
 M_{sample} is the mass of sample (g, usually 1 g, section I7.1.1, I7.2.1).

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed. In addition, the reporting of results may also need to take into account whether results are calculated on an air-dried basis (for example at 30 °C) or on a dry weight basis (at 105 °C).

When an air-dried sample is prepared, and from this say A % of inert extraneous material is removed, then if (excluding inert extraneous material)

moisture content on air-dried matter = B %

and

metal concentration on air-dried matter = C mg/kg

then

metal concentration on dry weight basis = $(C \times 100) / (100 - B)$ mg/kg

If the inert extraneous material needs to be taken into account, then

metal concentration on air-dried matter = $(C \times (100 - A)) / 100$ mg/kg

and

metal concentration on dry weight basis = $((C \times 100) / (100 - B)) \times ((100 - ((A \times 100) / (100 - B))) / 100)$ mg/kg

Table I1 Performance data

Table I1.1 250 ml Glass Tube Digestion Method

Certified Reference Material	CRM value (mg/kg)	Mercury	
		Bias (%)	RSD (%)
LGC6135 (ERM-CC6135)	3.2	1.6	4.8
LGC6138	1.5	-16.6	6.4
LGC6144	0.53	-8.0	12.0

Table I1.2 50 ml Plastic Tube Digestion Method

Reference Material	CRM value (mg/kg)	Mercury		LOD (mg/kg)
		Bias (%)	RSD (%)	
CMI 7002	0.085	2.4	8.3	0.03
CRM 052-050	0.815	-4.9	11.5	
CRM 037-050	30.7	-17.3	9.2	

Performance data provided by Environment Agency's National Laboratory Service

LOD is calculated as $2t_{0.05}\sqrt{2}$ times the within batch standard deviation of a blank clean sand (RTC-CLNSAND4) following analysis of 11 batches in duplicate.

LGC 6135 (ERM-CC135a) is a dried ground sieved (<100 µm) homogenised contaminated brick works soil

LGC 6138 is a dried ground sieved (<200 µm) homogenised coal-carbonisation site soil

LGC 6144 is a dried ground sieved (<200 µm) homogenised gas works contaminated soil

CMI 7002 is a dried ground sieved (<100 µm) homogenised light sandy soil

RTC CRM 052-050 is a dried sieved and homogenised loamy clay

RTC CRM 037-050 is a dried sieved and homogenised sandy loam

Results with a high bias may indicate that the CRM value may need to be checked (for example total or extractable value and methodology used to generate the reference value) or that the procedure used for that element may be inappropriate for the determination of that element in the matrix.

J The determination of selenium in soils and solid waste samples by *aqua regia* extraction using hydride generation atomic fluorescence spectrometry

J1 Performance characteristics of method

J1.1	Substance determined	Selenium.
J1.2	Type of sample	Soil, contaminated land and other solid waste samples.
J1.3	Basis of method	Selenium in soils, contaminated land or solid waste samples are extracted with <i>aqua regia</i> and diluted with water. Selenium compounds are reduced to Se(IV) and reacted with hydrogen to produce selenium hydride (SeH ₄) which is then determined by atomic fluorescence spectrometry.
J1.4	Range of application	Up to 1.5 mg/kg for selenium. Calibration range may be extended by taking a smaller aliquot (J7.3.1) of the <i>aqua regia</i> extract solution or diluting the <i>aqua regia</i> extract.
J1.5	Performance data	See Table J1.
J1.6	Interferences	The high acid strength overcomes most interferences. However, fatty compounds or surfactants can cause problems with foaming in the gas/liquid separator. This may be overcome by diluting the sample.

J2 Principle

Metals are extracted from dried, ground soils, contaminated land and other solid waste samples by the addition of *aqua regia*, followed by heating using a digestion block. The extract is cooled and made to volume with water. Hydrochloric acid, which reduces Se⁶⁺ to Se⁴⁺ is added to an aliquot of sample in a tube and placed in a water bath at 90 °C. The Se⁴⁺ is then reacted with hydrogen (generated by the acidification of sodium borohydride) to produce selenium hydride, SeH₄. Selenium is quantified by removal of the gas from the solution, by a stream of argon and carried to a cell illuminated by a selenium lamp with a fluorescence detector at a wavelength of 196 nm.

J3 Hazards

Appropriate personal protective equipment should be worn when handling reagents and potentially contaminated or hazardous samples. Concentrated acids should always be added to water and the operation carried out in a fume cupboard. The extract solutions contain concentrated acids and should be handled with care.

J4 Reagents

All reagents should be of sufficient purity so that they do not give rise to significant interference in the analysis. These should be checked for each batch of chemicals and reagents and verified by running reagent blanks with each batch of samples analysed. Reagents should be stored in sealed containers or other suitable vessels, stored at room temperature and kept in the dark, if necessary.

Water should be deionised (specific conductivity of less than 10 $\mu\text{S}/\text{cm}$) and volumetric glassware should be of at least grade B quality (preferably grade A). All reagents should be appropriately labelled, including the expiry date of the reagent. The preparation of these reagents should be recorded.

J4.1 Concentrated nitric acid (SG 1.42).

J4.2 Concentrated hydrochloric acid (SG 1.18).

J4.3 Sodium borohydride reagent (0.7 % w/v). In a fume cupboard, to a 2000-ml plastic beaker containing 1000 ml of water, add 4.0 g of sodium hydroxide and 7.5 g of sodium borohydride. Stir the solution until dissolved. Store in a high density plastic bottle. This solution should be prepared on the day of use.

J4.4 Hydrochloric acid (50 % v/v). In a fume cupboard, to a 1000-ml measuring cylinder containing 500 ml of water, carefully add 500 ml of hydrochloric acid (J4.2). Allow the solution to cool, mix well, and store in a glass or high density plastic bottle. This solution may be stored at room temperature for up to one month.

J4.5 Calibration stock solution (1000 mg/l). Stock solution containing 1000 mg/l of selenium is usually available commercially and may be stored at room temperature for up to twelve months.

J4.6 Intermediate calibration stock solution 1 (50 mg/l). To a 100-ml volumetric flask containing 50 ml of water, add 1.0 ml of nitric acid (J4.1) and 5.0 ml of selenium calibration stock solution (J4.5). Make to volume with water and mix well. This solution may be stored at room temperature for up to six months.

J4.7 Intermediate calibration stock solution 2 (1000 $\mu\text{g}/\text{l}$). To a 100-ml volumetric flask containing 50 ml of water, add 1.0 ml of nitric acid (J4.1) and 2.0 ml of intermediate calibration stock solution 1 (J4.6). Make to volume with water and mix well. This solution may be stored at room temperature for up to three months.

J4.8 Calibration blank solution. To a 100-ml volumetric flask containing 50 ml of water, add 1.0 ml of nitric acid (J4.1). Make to volume with water and mix well. This solution should be prepared on the day of use.

J4.9 Calibration solution 1 (7.5 $\mu\text{g}/\text{l}$). To a 100-ml volumetric flask containing 50 ml of water, add 1.0 ml of nitric acid (J4.1) and 0.75 ml of intermediate calibration stock solution 2 (J4.7). Make to volume with water and mix well. This solution should be prepared on the day of use.

J4.10 Calibration solution 2 (15 µg/l). To a 100-ml volumetric flask containing 50 ml of water, add 1.0 ml of nitric acid (J4.1) and 1.5 ml of intermediate calibration stock solution 2 (J4.7). Make to volume with water and mix well. This solution should be prepared on the day of use.

J4.11 Independent AQC solutions. These solutions provide an independent check of the calibration.

J4.12 AQC stock solution A (1000 mg/l). Stock solution containing 1000 mg/l of selenium is usually available commercially and may be stored at room temperature for up to twelve months.

J4.13 AQC stock solution B (10 mg/l). To a 100-ml volumetric flask containing 50 ml of water, add 5.0 ml of nitric acid (J4.1) and 1.0 ml of AQC stock solution A (J4.12). Make to volume with water and mix well. This solution may be stored at room temperature for up to six months.

J4.14 AQC stock solution C (500 µg/l). To a 100-ml volumetric flask containing 50 ml of water, add 1.0 ml of nitric acid (J4.1) and 5.0 ml of AQC selenium stock solution B (J4.13). Make to volume with water and mix well. This solution may be stored at room temperature for up to one month.

J4.15 Working AQC solution (10 µg/l). To a 100-ml volumetric flask containing 50 ml of water, add 1.0 ml of nitric acid (J4.1) and 2.0 ml of AQC selenium stock solution C (J4.14). Make to volume with water and mix well. This solution should be prepared on the day of use.

J4.16 AQC soil. A laboratory reference material comprising a spiked soil should be used for AQC purposes for *aqua regia* extracted samples.

J4.17 Dilution solution. To a 500-ml volumetric flask containing 100 ml of water, add 5.0 ml of nitric acid (J4.1). Make to 500 ml with water and mix well. This solution may be stored at room temperature for up to one month.

J5 Apparatus

Cleanliness is an essential requirement for all extractions of trace metals from soil, contaminated land and other solid waste samples. Glassware should be washed using a detergent solution, for example Decon 90, and rinsed with water. The glassware should then be soaked in dilute nitric acid solution for at least 24 hours before use and rinsed thoroughly with water.

J5.1 Top pan balance capable of weighing to ± 0.01 g.

J5.2 250 ml glass digestion tubes with associated glass reflux condensers or 50 ml plastic digestion tubes with associated glass cold finger condensers.

J5.3 Thermostatically controlled temperature digestion block capable of maintaining a temperature of 160 °C.

- J5.4 Thermostatically controlled temperature digestion block capable of maintaining a temperature of 120 °C.
- J5.5 Volumetric flasks (grade B or better) - 100-ml, 500-ml, capacity.
- J5.6 Measuring cylinder - 1000-ml capacity.
- J5.7 Plastic beaker – 2000 ml capacity.
- J5.8 Dispensers - 0.1 ml to 10 ml capacity.
- J5.9 Centrifuge, syringes, 0.45um cartridge filters.
- J5.10 Hydride generation equipment, selenium hollow cathode discharge lamp, fluorescence detection system with auto-sampler and with instrument control and data handling system.
- J5.11 15 ml plastic tubes, auto-sampler plastic cups (27 ml) and pump tubes.
- J5.12 Gases: Argon >99.99 %.

J6 Sample preparation

Soil, contaminated land and other solid waste samples should be air-dried at less than 30 °C. The loss on drying should be recorded. For example, spread a portion of sample onto a tray and place the tray in an oven (set at less than 30 °C) until dry, for example overnight or for a longer time if necessary. Using a plastic spatula, gently break up any lumps. Any large rocks, bricks and other inert material greater than 10 mm should be hand picked and removed. Record the total weight of any discarded material. The sample should then be sieved through a 10 mm sieve. (Soil being assessed for disposal to land for agricultural purposes need not undergo sieving through the 10 mm sieve but should be sieved through a 2 mm sieve). The sieved sample should then be jaw-crushed, if required, and ball-milled using agate pots and balls to obtain a homogeneous fraction for subsequent extraction and analysis. (If the material is very hard then a tungsten carbide milling system should be used). The prepared sample should be stored in an air-tight plastic container.

J7 Analytical procedure

Step	Procedure	Note
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J7.1 250 ml Glass Tube Sample Digestion

J7.1.1 Weigh out 1.0 g of the prepared air-dried and ground sample (J6) into an anti-static weighing boat. Transfer the sample to a 250 ml glass digestion tube and reweigh the weighing boat, record the weight of sample, see note a.

(a) An AQC soil sample and blank sample should be similarly weighed.

J7.1.2 Place the tube in a fume-extracted area and carefully add 2.5 ml of concentrated nitric acid (J4.1) followed by 7.5 ml of concentrated hydrochloric acid (J4.2) see note b. Cover the tube loosely, for example with polyethylene film material and allow the sample to stand at room temperature in a fume-extracted area for a minimum of eight hours, see note c.

J7.1.3 Switch on the heating block and reflux condenser re-circulating water bath. Place the tube into the heating block and connect the reflux water condenser. Start the heating block digestion program, see note d. After heating, allow the solution to cool.

J7.1.4 Rinse down the inside of the condenser with a small portion of water, and allow the water to drain into the digestion tube. Quantitatively transfer the contents of the digestion tube into a 50 ml plastic centrifuge tube. Rinse the digestion tube with water and transfer the rinsings to the centrifuge tube. Make to 50 ml with water, mix well and then allow sample to stand, see note e.

J7.2 50 ml Plastic Tube Sample Digestion

J7.2.1 Weigh out 1.0 g of the prepared air-dried and ground sample (J6) into an anti-static weighing boat. Transfer the sample to a 50 ml plastic digestion tube and reweigh the weighing boat, record the weight of sample. See note a.

J7.2.2 Place the tube in a fume-extracted area and carefully add 2.5 ml of concentrated nitric acid (J4.1) followed by 7.5 ml of concentrated hydrochloric acid (J4.2). See note b. Cover the tube loosely with a lid. Allow the sample to stand at room temperature in a fume-extracted area for a minimum of eight hours, see note c.

J7.2.3 Place the tube in the digestion block, remove the lid and place a glass cold-finger condenser over the tube. Switch on the heating block and start the heating block digestion program, see note f. After heating, allow the solution to cool.

(b) Care should be taken, as samples that contain a high carbonate content will effervesce.

(c) The sample may be left overnight at this stage.

(d) For example the following programme has been found suitable:
60 °C for 10 minutes,
80 °C for 10 minutes,
100 °C for 10 minutes,
160 °C for 2 hours, and finally,
30 minutes cooling time.

(e) On standing, most samples will settle to give a clear solution. If not, centrifuge the suspension or filter using a syringe and 0.45 µm filter cartridge.

(f) For example the following programme has been found suitable:
linear temperature ramp from room temperature to 120 °C in 50 minutes,
hold at 120 °C for 150 minutes, and finally, allow to cool.

J7.2.4 Rinse down the condenser with a small portion of water, and allow the water to drain into the digestion tube. Make to 50 ml with water, place a lid on the tube, mix well and then allow sample to stand, see note e.

J7.3 Se⁴⁺ oxidation state generation

J7.3.1 Dispense 3.5 ml of extract solution (J7.1.4 or J7.2.4) into a 15 ml disposable centrifuge tube, add 3.5 ml of dilution solution (J4.17) and cover the tube loosely, for example with polyethylene film material. See note g.

(g) Whatever aliquot volume is taken, this should, where appropriate, be made to 7.0 ml with dilution solution (J4.17).

Dispense 3.5 ml of blank extract solution into a 15 ml disposable centrifuge tube, add 3.5 ml of dilution solution (J4.17) and cover the tube loosely, for example with polyethylene film material.

Dispense 1.40 ml of AQC solution (J7.15) into a 15 ml disposable centrifuge tube, add 5.60 ml of dilution solution (J4.17) and cover the tube loosely, for example with polyethylene film material.

Dispense 7.0 ml of calibration solutions (J4.8 - J4.10) into separate 15 ml disposable centrifuge tubes and cover the tubes loosely, for example with polyethylene film material.

J7.3.2 To each tube add 7.0 ml hydrochloric (J4.2). Place the tubes in a water bath set at 90 °C and leave for between 10 and 15 minutes. See note h.

(h) This ensures the solution in the tube reaches at least 70 °C.

J7.4 Hydride generation atomic fluorescence selenium determination

J7.4.1 Following the manufacturer's instructions, set up the hydride generation, atomic fluorescence instrument. See note i.

(i) Ensure the sodium borohydride reagent (J4.3) reservoir and the 50 % hydrochloric acid (J4.4) reservoir are full and the argon flow is set correctly.

J7.4.2 Perform instrument system suitability checks to verify instrument performance.

J7.4.3 Calibrate the instrument using the calibration solutions (J7.3) see note j.

(j) If required, the calibration may be checked, by running the AQC solution (J4.15) prior to sample analysis.

J7.4.4 Analyse the blank, AQC solution, sample blank, AQC soil sample and sample extracts (J7.3) at the appropriate frequency. Between each sample the system should be set to rinse using the water. See notes k and l.

(k) The instrument may be re-calibrated as required to maintain performance.

(l) For samples with concentrations exceeding the calibration range, the extract solution (J7.1.4, J7.2.4) should be appropriately diluted with dilution solution (J4.17) or a smaller aliquot (J7.3.1) taken and the determination repeated. Alternatively, repeat the extraction with a smaller quantity of sample (J7.1.1, J7.2.1) or use more *aqua regia* and make to a larger volume (J7.1.4, J7.2.4) if appropriate.

J8 Calculations

The concentration of the element in the sample is given by:

$$C_{\text{sample}} = (C_{\text{extract}} \times V_{\text{extract}} \times V_{\text{oxidation}} \times \text{DF}) / M_{\text{sample}} \times V_{\text{aliquot}}$$

Where C_{sample} is the concentration of the element in the air-dried sample (mg/kg);
 C_{extract} is the concentration of element in the sample extract solution (mg/l);
 V_{extract} is the volume of extract (ml, usually 50 ml, section J7.1.4, J7.2.4);
 $V_{\text{oxidation}}$ is the oxidation volume (section J7.3.1, usually 7 ml);
 V_{aliquot} is the aliquot volume of extract (note g of J7.3.1);
DF is the dilution factor, if any (note l, section J7.4.4); and
 M_{sample} is the mass of sample (g, usually 1 g, sections J7.1.1 and J7.2.1).

For samples where inert extraneous material (for example stones and bricks) is removed prior to analysis, results may be reported with or without taking account of this material removed. In addition, the reporting of results may also need to take into account whether results are calculated on an air-dried basis (for example at 30 °C) or on a dry weight basis (at 105 °C).

When an air-dried sample is prepared, and from this say A % of inert extraneous material is removed, then if (excluding inert extraneous material)

moisture content on air-dried matter = B %

and

metal concentration on air-dried matter = C mg/kg

then

metal concentration on dry weight basis = $(C \times 100) / (100 - B)$ mg/kg

If the inert extraneous material needs to be taken into account, then

$$\text{metal concentration on air-dried matter} = (C \times (100-A))/100 \text{ mg/kg}$$

and

$$\text{metal concentration on dry weight basis} = ((C \times 100)/(100-B)) \times ((100 - ((A \times 100)/(100-B)))/100) \text{ mg/kg}$$

Table J1 Performance data

Table J1.1 250 ml Glass Tube Digestion Method

Certified Reference Material	CRM value (mg/kg)	Selenium	
		Bias (%)	RSD (%)
LGC6135 (ERM-CC6135)	0.9	14.1	1.7
LGC6138	1.5	13.6	3.0
LGC6144	0.71	3.6	3.5
LGC6180	2.5	-6.3	5.8
GBW07405	1.6	0.6	4.1

Table J1.2 50 ml Plastic Tube Digestion Method

Certified Reference Material	CRM value (mg/kg)	Selenium		LOD (mg/kg) 0.1
		Bias (%)	RSD (%)	
CRM 039-050	220	0.0	9.3	
CRM 048-050	137	-2.9	6.9	
CRM 051-050	165	-2.5	9.1	

Performance data provided by Environment Agency's National Laboratory Service

LOD is calculated as $2t_{0.05}\sqrt{2}$ times the within batch standard deviation of a blank clean sand (RTC-CLNSAND4) following analysis of 11 batches in duplicate.

LGC 6135 (ERM-CC135a) is a dried ground sieved (<100 µm) homogenised contaminated brick works soil

LGC 6138 is a dried ground sieved (<200 µm) homogenised coal-carbonisation site soil

LGC 6144 is a dried ground sieved (<200 µm) homogenised gas works contaminated soil

LGC 6180 is a dried ground sieved (<250 µm) homogenised pulverised fuel ash

GBW07405 is a dried ground sieved homogenised soil from China

RTC CRM 039-050 is a dried sieved and homogenised loam

RTC CRM 048-050 is a dried sieved and homogenised sand

RTC CRM 051-050 is a dried sieved and homogenised clay

Results with a high bias may indicate that the CRM value may need to be checked (for example total or extractable value and methodology used to generate the reference value) or that the procedure used for that element may be inappropriate for the determination of that element in the matrix.

Address for correspondence

However well procedures may be tested, there is always the possibility of discovering hitherto unknown problems. Analysts with such information are requested to contact the Secretary of the Standing Committee of Analysts at the address given below. In addition, if users would like to receive advanced notice of forthcoming publications please contact the Secretary on the Agency's web-page.

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