Methods for the Determination of Metals in Soils, Sediments and Sewage Sludge and Plants by Hydrochloric-Nitric Acid Digestion, with a note on the Determination of the Insoluble Metal Contents 1986

Methods for the Examination of Waters and Associated Materials

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Contents

About this Series		3
Warning to Users		4
Introduction		5
A	**Determination of Acid Soluble, Cadmium, Chromium, Copper, Iron, Lead, Manganese, Mercury, Nickel and Zinc in Soils, Sediments and Sewage Sludge following Reflux Digestion with a Hydrochloric and Nitric Acid Mixture**	8
A1	Performance Characteristics of the Method	8
A2	Principle	10
A3	Interferences	10
A4	Hazards	11
A5	Reagents	11
A6	Apparatus	12
A7	Analytical Procedure	13
A8	Optimization of Instrumental Conditions	15
A9	Checking the Linearity of Calibration Curves	15
A10	Change of Concentration Range of the Method	15
A11	Sources of Error	15
A12	Analysis of Peats, Peaty Soils, and Plants	16
A13	Checking the Accuracy of Analytical Results	16
B	**Solution of Residues Insoluble in Hydrochloric-Nitric Acid**	17
B1	Introduction	17
B2	Elements likely to be brought into solution	17
B3	Outline	17
B4	Hazards	17
B5	Reagents	17
B6	Apparatus	17
B7	Analytical Procedure	18

C	**The Determination of Acid Soluble Aluminium, Cadmium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Silver and Zinc in Sewage Sludges by Atomic Absorption Spectrophotometry following Digestion with a Hydrochloric and Nitric Acid Mixture**	20
C1	Performance Characteristics of the Method	20
C2	Principle	22
C3	Interference	23
C4	Hazards	23
C5	Reagents	23
C6	Apparatus	23
C7	Sample Collection of Preservation	24
C8	Determination of the Percentage of Dry Solids and Preparation of the Dried Sludges	24
C9	Analytical Procedure	24
C10	Optimization of Instrumental Conditions	26
C11	Checking the Linearity of Calibration Curves	26
C12	Changing the Concentration Range of the Method	26
C13	Sources of Error	26
C14	Checking the Accuracy of Analytical Results	26
D	**The Determination of Acid Soluble Cadmium, Chromium, Copper, Lead, Manganese, Nickel and Zinc in Soils by Atomic Absorption Spectrophotometry following Digestion with a Hydrochloric and Nitric Acid Mixture**	27
D1	Performance Characteristics of the Method	27
D2	Principal	28
D3	Interferences	29
D4	Hazards	29
D5	Reagents	29
D6	Apparatus	29
D7	Sample Collection of Preservation	29
D8	Preparation of Soil for Analysis	30
D9	Analytical Procedure	30
D10	Optimization of Instrumental Conditions	31
D11	Checking the Linearity of Calibration Curves	31
E	**Estimation of the Accuracy of Analytical Results for Variants of the Methods**	32
E1	Introduction	32
E2	Basis of Suggested Tests	32
E3	Evaluation of Results	32
E4	Detection of Interference	33
References		34
Addendum to Chromium in Raw and Potable Waters and Sewage Effluents		36
Address for Correspondence		36
Members Responsible for this Method		inside back cover

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About this series

This booklet is part of a series intended to provide both recommended methods for the determination of water quality, and in addition, short reviews of the more important analytical techniques of interest to the water and sewage industries.

In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as series of booklets on single or related topics; thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods and notes being issued when necessary.

The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users – the senior technical staff to decide which of these methods to use for the determination in hand. Whilst the attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has seven Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General non metallic substances
6.0 Organic impurities
7.0 Biological methods
9.0 Radiochemical methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover. Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No. 5.

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in that booklet.

L R PITTWELL
Secretary

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Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary.

Local Safety Regulations must be observed.

Laboratory procedures should be carried out only in properly equipped laboratories.

Field Operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried.

Care should be taken against creating hazards for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

Lone working, whether in the laboratory or field, should be discouraged.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Guide to Safe Practice in Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection', Public Health Laboratory Service Monograph 6, HMSO, London.

It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio-chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.

Introduction

Use of these methods

A knowledge of the metal content of sludge is important as a guide to the input of metals to a sewage works and for monitoring sludge disposal to land or sea. Metal contents of soils are also required to monitor sludge disposal and to decide upon rates of sludge application to agricultural land. This booklet and associated booklets in this series give methods for the determination of traces of some metals in soils and sludges. Other similar booklets in the series give methods for the determination of other materials such as organic pesticides in the same materials (Refs 23–35).

The underlying analytical problem is that soils and, to some extent, sludges are complex mixtures of both organic and inorganic materials, not all of which may contain the determinand at all, or only contain it in a form not readily available to plants grown in that soil or in soil treated with that sludge. Furthermore, plants vary both in their ability to pick up the different metals and in their reaction to them once picked up. Hence a variety of extraction tests have been developed (Refs 22 and 39). For easily decomposed samples a simple nitric acid digestion procedure has already been published in this series (Ref 4).

This booklet contains four basic procedures. The first (A) was developed principally for the determination of metals in soils and sediments; but can also be used for the analysis of liquid and solid sewage sludges. As some minerals in soils and sediments are insoluble in hot hydrochloric-nitric acid mixtures, a hydrofluoric acid digestion procedure (B) is appended which can be used for the determination of metals in such insoluble residues where required. Similar procedures but with a shorter digestion time have also been developed for (C) the analysis of dried sludges, which can be adapted for the analysis of wet sludges and (D) for many soils. As the ultimate test of whether or not a crop grown in a certain soil will pick up a metal from it is to grow some in that soil and in a control soil and compare analyses, some information on plant analysis is also given.

Various final quantification steps may be used and metals other than cadmium, chromium, copper, iron, lead, manganese, nickel and zinc may be determined by method A; but test data for only the determination of the above metals by atomic absorption spectrophotometry has been given. It was not practicable for the panel to evaluate all the elements which may be determined by this method, nor was it possible to evaluate all the possible methods of quantification that could be used. Analysts wishing to determine other metals or to use other methods of quantification such as inductively coupled plasma emission spectroscopy, after the digestion steps, should evaluate their procedure thoroughly before use.

Method of evaluation

As the extractability of a substance from soil depends on the form in which it is present in or bound to that soil, when evaluating a method, remember that test samples prepared simply by mixing the matrix and either the determinand or a compound of the determinand may not give a true evaluation, unless the addition can be incorporated into the sample in the same form as that in which it would normally be present. Even then, care must be taken that interference effects relating to the quantification stage are not overwhelmed. For a thorough investigation of the digestion stage, samples of known composition can be carried through the method. Reference materials, 3 soils and 3 sludges, certified for total contents and with reliable (uncertified) mean values for $HCl–HNO_3$ digest contents are available for this purpose from the Community Bureau of Reference (CBR) in Brussels. Alternatively the efficiency of extraction should be checked, as it was for cobalt in method A, by examining any residue, tests should also be made by collecting and analysing fumes given off to see whether there are volatility losses. Analysis of residues either entails use of solid sample analytical methods such as XRF (19) or Arc Emission (18); see

also (42) or the use of more severe digestion processes such as method B in this booklet. Thereafter tests on the quantification steps are relatively easy and can be made on synthetic solutions.

A few already published methods for the determination of specific metals do contain sections on sludge analysis (Refs 35, 36, 37 and 38).

Summary of Capabilities of these methods

Digestion A

(i) Strongly oxidizing, very acidic comparable with perchloric acid.
(ii) Will not dissolve highly acid resistant non oxidizable minerals. See Section A1.12.
(iii) There is a slight risk of loss of elements with volatile chlorides and acids.
(iv) Samples with very high contents of organic matter can prove troublesome due to foaming. If a prior ignition is added some readily volatile elements will be lost. For some, such as molybdenum, whether such loss occurs is dependent on the furnace atmosphere, thus molybdenum is readily lost under oxidizing conditions as the trioxide, but not as the dioxide under mildly reducing conditions. See Section A12.

Digestion B

(i) Coupled with a previous digestion A this procedure will dissolve almost all metals. See Section B1.
(ii) In addition to the slight risk of loss mentioned in A(iii) above, care is needed, if the element has a volatile fluoride, not to decompose fluorocomplexes formed in the digestion.

Digestions C and D

(i) Not as severe as procedure A and far less severe than A plus B; but is usually sufficient for ordinary samples. If in doubt a comparison should be made prior to deciding which method to use routinely.

General

Digestions A, C and D are suited to samples requiring oxidation or acidification in order to dissolve, or which will readily ion-exchange with hydrogen ion.

Digestion B is intended for complex aluminosilicate, aluminate and silicate minerals and similar.

The criteria governing the success of a digestion procedure are:

(i) the ability either to dissolve the sample, or quantitatively to leach out the determinand,
(ii) without loss by volatilization or precipitation.

The following table lists the determinands for which some test data is given directly or by reference in the various methods. Some extra information on the methods of determination is also included.

Metal etc	See Procedure or Reference	Remarks
Aluminium	A, B, C	*
Arsenic	B, 35, 40	Poor precision in A C and D* (MAFF and YWA information)
Barium	B	*
Boron	B, 32	
Cadmium	A, C, D, 4, 22	*
Calcium	A, B, C	*
Chromium	A, B, C, D, 4	Needs a nitrous oxide flame for determination by AAS
Cobalt	A, B, C	
Copper	A, B, C, D, 4, 22	
Iron	A, B, C, 20	
Lead	A, B, C, D, 4, 22	*
Lithium	B	*
Magnesium	A, B	*
Manganese	A, B, C, D, 20, 22	
Mercury	A, C, 36	Atomic Fluorescence Spectrophotometry is preferred * (MAFF information)
Molybdenum	C, 37	
Nickel	A, B, C, D, 4, 22	
Phosphorus	B, 31	
Potassium	A, B	
Selenium	35	*
Silicon	B, 16	
Silver	C, 38	
Strontium	B	*
Zinc	A, B, C, D, 22	

* New or revised booklets in this series on the determination of these metals are in draft at the time of going to press.

A Determination of Acid Soluble Cadmium, Chromium, Copper, Iron, Lead, Manganese, Mercury, Nickel and Zinc in Soils, Sediments and Sewage Sludges following Reflux Digestion with a Hydrochloric and Nitric Acid Mixture

A1 Performance Characteristics of the Method

A1.1	Substances determined	Acid soluble cadmium, chromium, copper, mercury, iron, lead, nickel, manganese and zinc.
A1.2	Type of sample	Soils, sediments and sewage sludges.
A1.3	Basis of the method	Digestion of the sample with hydrochloric-nitric acid mixture followed by determination of the extract metals by atomic absorption spectrophotometry. See Section A1.12.
A1.4	Range of application for soils (3 g sample) (Without dilution of digest or rotation of the burner)	Cadmium 0.7 –70 mg/kg dry weight Chromium 3 –330 mg/kg dry weight Copper 1.7 –330 mg/kg dry weight Iron 33 –830 mg/kg dry weight Lead 3 –330 mg/kg dry weight Manganese 7 –170 mg/kg dry weight Nickel 3 –330 mg/kg dry weight Zinc 1.7 –70 mg/kg dry weight Mercury 0.04–10+mg/kg dry weight (by AFS) Dilution of the digest solutions will normally be necessary for the determination of iron, manganese and occasionally zinc in soils. See Section A10.
A1.5	Calibration curve	Linear over the concentration ranges given in Section A1.4.

A1.6 Standard deviation

	Metal	Concentration (mg/kg dry weight	Total standard deviation (mg/kg)
Three sewage sludges (a)	Cadmium	2.8–71	0.68–2.52
	Chromium	92–860	3.76–14.4
	Copper	400–880	9.4–10.2
	Lead	300–1170	3.2–16.3
	Manganese	190–490	12.9–17.8
	Nickel	38–940	2.2–7.8
	Zinc	3030–3430	85.7–131
Seven contaminated soils (a)	Cadmium	<1.7–29	0–1.51
	Chromium	33.2–240	0.58–5.72
	Copper	21–230	0.36–5.93
	Lead	20–1220	0.5–24.1
	Manganese	300–840	12–23.4
	Nickel	13–94	0.87–2.40
	Zinc	81–1420	1.18–16.5

Ten uncontaminated soils (a)	Cadmium	*0.07–0.39	0.003–0.038
	Chromium	9.2–171	0.56–7.16
	Copper	4.3–5.6	0.15–1.11
	Iron	9600–65600	214–1435
	Lead	4.2–44	0.15–1.43
	Manganese	138–837	3.6–132
	Nickel	<3.4–7.4	0–1.45
	Zinc	16–157	0.27–4.44

* The detection limit and the range of application can be improved by use of the more sensitive atom-trapping technique which was used for the analysis of cadmium in the uncontaminated Soils (1).

		3 sewage sludges	7 contaminated soils	4 Canadian reference soils	6 uncontaminated soils
Mean relative standard deviations (a)	Cd	3.7	4.1	19	9.3
	Cr	2.7	2.9	6.4	5.5
	Cu	1.7	2.2	2.7	4.8
	Fe	—	—	2.3	2.1
	Pb	1.9	4.7	8.2	5.2
	Mn	5.5	4.2	2.2	8.0
	Ni	3.0	6.3	3.4	7.0
	Zn	3.1	2.6	2.4	2.9

	Reference sewage sludge	Mean Hg mg/kg	Sw mg/kg	
	BCR 144	1.35	0.105	All with 4 degrees of freedom (b)
	BCR 145	8.2	0.38	
	BCR 146	8.5	0.22	

A1.7	Limit of detection (expressed as mg/kg dry weight)	Cadmium 0.7, chromium 3, copper 1.7, iron 33, lead 3, manganese 7, nickel 3 and zinc 1.7 mg/kg (a), mercury 0.04 mg/kg (b).
A1.8	Sensitivity (for 1%)	Cd 0.7, Cr 6, Cu 1.7, Fe 33, Pb 4, Mn 7, Ni 3 and Zn 1.7 mg/kg.
A1.9	Bias	See A1.12
A1.10	Interferences	See Section A3.
A1.11	Time required for analysis	Starting from dry, prepared samples, the analytical time for 12 samples (excluding the overnight standing period) is approx. 8 hours. For eight elements to be determined by flame atomic absorption with associated calibration standards the analytical time is approx. 4 hours.

(a) These data were obtained at the Department of Spectrochemistry, The Macaulay Institute for Soil Research, Craigiebuckler, Aberdeen. For full details see Reference (1). Each sludge was analysed in duplicate five times and each soil separately five times. All the performance characteristics apply to dried samples.
(b) MAFF Fisheries Laboratory, Burnham-on-Crouch.

A1.12 Completeness of the Digestion

The reflux digestion with a mixture of hydrochloric and nitric acids does not determine the total metal content but some 70 to 90 per cent of the total contents of cadmium, chromium, copper, iron, lead, manganese and zinc are extracted from uncontaminated topsoils and an even greater proportion from sludge contaminated soils (1).

Analysis of the siliceous residues remaining after acid digestion of seven contaminated soils by direct current arc spectrographic analysis confirmed that most of the copper, lead and manganese had been removed.

In order to investigate the degree of breakdown and dissolution of soil minerals, analysis of four Canadian standard reference soils (2) which have certified values for the true total contents of a number of elements has been carried out. Twenty-five uncontaminated Scottish topsoils derived from a wide range of parent materials were also analysed. The total contents of major elements in these soils had been previously determined by lithium metaborate fusion followed by dissolution and determination by atomic absorption spectrophotometry (3).

The mixed-acid extractable values expressed as a percentage of the true total contents are reported in Table 1 which shows the mean values obtained for four groups of soils. These data show the degree of mineral breakdown and dissolution of major elements in soils affected by the mixed acid digestion.

Table 1 Mean percentages of the total metal contents extractable by mixed acid reflux digestion.

Sample	4 Canadian Standard reference soils SO-1 to SO-4	6 Scottish topsoils	10 Scottish topsoils	9 Soil profile A-horizons
Metal	Percentage extracted			
Al	35	37	38	42
Ca	62	50	42	37
Fe	85	88	80	81
K	22	18	16	14
Mg	69	59	71	69
Na	4.1	4.7	2.6	2.7

About 85% of the iron, 70% of the magnesium, 50% of the calcium, 40% of the aluminium, 20% of the potassium and 4% of the sodium was extracted. It appears that the more easily disrupted ferromagnesian minerals in the soil are broken down by the digestion, while more stable aluminosilicates such as feldspars are not. Much of the total contents of some of the biologically important trace elements including Cr, Cu, Pb, Cd, Mn and Zn are contained in the ferromagnesian minerals and are therefore released during the digestion.

A bias due to incomplete extraction of trace metals is therefore introduced using this digestion procedure but this is relatively small and of little importance in the context of sewage sludge application to agricultural land. However the alternative digestion procedure using hydrofluoric acid will bring most of this residue into solution, and eliminate the bias, but at slightly poorer precision due to losses during sample transfer.

No performance date for iron in sewage sludges are reported (Section A1.6) because iron and also manganese are not elements of concern as potential pollutants arising from sewage sludge disposal. The extraction procedure is also satisfactory for cobalt though no performance characteristics are available for this element. Acid insoluble residues remaining after digestion have been analysed by d-c carbon arc emission spectrography and no cobalt could be detected. Results of analysis of over two hundred soils by the mixed acid procedure and by arc emission spectrography show that at least 85% of the total cobalt is extracted.

A2 Principle

The finely ground sample or dried liquid sludge is digested by standing overnight (at least 16 hours) at room temperature with a hydrochloric/nitric acid mixture and then boiled gently under reflux for 2 hours. The digest is then filtered, made up to volume with 2M nitric acid and the metals determined by atomic absorption spectrophotometry.

A3 Interferences

A3.1 No specific tests for the possible effects of other substances on the determination of these metals by this method, which involves a nitric acid/hydrochloric acid

digestion procedure, have been carried out. Interelement effects in complex matrices such as sludge or soil digests are dependent upon the instrument and flame conditions, the choice of wavelength used, and the use of chemical releasing agents or matrix modifiers.

A3.2 When two sludges, digested using the rapid open-tube method with nitric acid only were analysed for cadmium, copper, lead, nickel and zinc by nine laboratories, satisfactory relative standard deviations were obtained and comparison of results obtained within laboratories using air/acetylene and nitrous oxide/acetylene flames indicated negligible interference effects (4). However, significant interelement effects were found for chromium determinations in the air/acetylene flame. The degree of interference was dependent on instrumental conditions and typically it can be reduced to ±20% using an acetylene-rich non-luminous flame. These effects can be further minimized by the use of the nitrous oxide/acetylene flame provided 1000 mg/l potassium ion is added to the digestion to suppress ionization. Problems have also been encountered with iron and manganese (20).

A3.3 When ten soils were digested in nitric acid/hydrochloric acid and analysed the results obtained when using a nitrous oxide/acetylene flame for chromium were on average 75% higher than when using an acetylene-rich non-luminous flame and for manganese were on average 16% higher than when using an air/acetylene flame. The use of the hotter nitrous oxide/acetylene greatly reduces interference effects in the determination of chromium, manganese and iron and should be used for determining these three elements in all types of sample and particularly soils and sediments (3). If a nitrous oxide/acetylene flame is not available the air/acetylene flame could be used for determining chromium, manganese and iron in sludge samples only where there is a lower concentration of matric elements, in which case the performance characteristics quoted in Section 1 would no longer apply.

A3.4 For all elements determined at a wavelength of less than 300 nm a background correction should be used. If interferences are suspected then the method of standard additions should be used. Regular quality control checks and analysis of standard reference materials should be carried out (see Section A12).

A4 Hazards

Digestions with hydrochloric and nitric acids are potentially hazardous. The digestions should be carried out in a well-ventilated fume cupboard with the reflux digestion on a temperature controlled heating apparatus. It is essential to add anti-bumping granules to the blank to prevent bumping. Wear safety goggles.

The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away. When a nitrous oxide-acetylene flame is to be used, ignition procedures, operating conditions and extinguishing procedure must be strictly adhered to.

A5 Reagents

Analytical reagent grade chemicals are suitable unless otherwise stated. All reagent and standard solutions should be stored in borosilicate glass or polyethylene bottles unless otherwise stated.

A5.1 Water

The water used to prepare the reagent and standard solutions should have negligible metal contents relative to the lowest concentration in the sample solutions. Water distilled from an all glass apparatus is normally suitable but deionized water may contain traces of metals depending upon the local water supply.

A5.2 Aluminium oxide or porous ceramic tile anti-bumping granules.

These should be soaked in 12.5% V/V nitric acid overnight, washed thoroughly with water, dried and stored in a dry bottle.

A5.3 Nitric acid (d_{20} 1.42) and (d_{20} 1.40)

Ultra high purity nitric acid is suitable without distillation. Analytical reagent grade nitric acid often contains unacceptably high concentrations of certain elements. Distillation of lower grade nitric acid from a suitable all-borosilicate glass apparatus

will produce an acid quality which compares very favourably with the highest grades available commercially. The distillation must be carried out in a fume cupboard and all necessary precautions taken. Nitric acid may be distilled directly but it is preferable to add 100 ml water per 1 litre of acid to reduce fumes in which case the nitric acid has a density of 1.40. A piece of porous unglazed ceramic tile or anti-bumping granules must always be present and a fresh piece must always be added prior to each subsequent distillation. Reject the initial and final portions (approx. 100 ml in each case) of the distillate.

A5.4 Nitric acid 12.5% V/V

Dilute 125 ± 2 ml of nitric acid (d_{20} 1.42) with water to 1 litre in a measuring cylinder.

A5.5 Hydrochloric acid 6M (d_{20} 1.10)

Ultra high purity acid is suitable without distillation. Dilute 260 ± 2 ml of ultra high purity hydrochloric acid (d_{20} 1.18) to 500 ml with distilled water. Analytical grade hydrochloric acid may also be distilled in a suitable all-borosilicate glass apparatus to produce a quality comparable with the highest grades available commercially. The distillation must be carried out in a fume cupboard and all necessary precautions taken. Mix anaytical grade hydrochloric acid (d_{20} 1.18) with water in the proportion 4:3 and distil. A piece of porous unglazed ceramic tile or anti-bumping granules must always be present and a fresh piece must always be added prior to each subsequent distillation. Reject the initial and final portions (approx. 100 ml in each case) of the distillate. A mixture of hydrochloric acid and water forms a constant boiling mixture and the distillate is 6M in concentration.

A5.6 Potassium solution (10% M/V)

Dissolve 19.1 ± 0.2 g potassium chloride (Analytical grade reagent) in water in a beaker. Transfer quantitatively to a 100 ml calibrated flask and dilute with water to the mark. Mix well. If potassium is to be determined, 10% M/V caesium (as chloride) can be used in place of potassium as an ionization suppressant.

A5.7 Metal standard solutions

Prepare separate 1000 mg/l standard solutions for each metal by dissolving 1.00 ± 0.001 g of the metal (purity greater than 99.9%) in 100 ± 1 ml of nitric (d_{20} 1.42) contained in a beaker. Transfer quantitatively to a 1-litre calibrated flask and dilute with water to the mark. Mix well. Alternativey, commercially available standards may be used.

A6 Apparatus

A6.1 Glassware

Use only borosilicate glassware. All new glass apparatus should be cleaned before use by filling with, or immersing in hot 12.5% V/V nitric acid overnight, and rinsing thoroughly with water. Thereafter a thorough rinse with 12.5% V/V nitric acid followed by a thorough rinse with water after each use is effective. It is recommended that one set of apparatus be reserved *solely* for metals-in-sludge and another set of apparatus *solely* for soil determinations, and each be suitably stored to avoid contamination. To maintain a check on the cleanliness of the apparatus use each set of glassware at random for the blank determination.

A6.2 Soil sieve

Field moist soils should be air dried, sieved and prepared as described in Part B of reference (5).

A6.3 Grinding mill

Preferably agate, capable of grinding dried soils, sludges and sediments to less than 150 μm size without contamination. For sludges only, an agate pestle and mortar may be suitable. See also ref 5.

A6.4 Temperature controlled heating apparatus

Suitable for heating 100 ml round bottom flasks equipped with water-cooled reflux condensers of about 40 cm in length with temperature control to facilitate gentle boiling. Other suitably controlled heating apparatus may be used.

A6.5 An atomic absorption spectrophotometer

The instrument must be equipped with an air-acetylene flame and with suitable hollow cathode lamps. A nitrous oxide/acetylene flame is required for the determination of chromium, iron and manganese. A background correction is required for all elements determined at a wavelength of less than 300 nm, namely cadmium, iron, lead, manganese, nickel and zinc. A general guide to the use of atomic absorption spectrophotometry is given in reference (6).

A7 Analytical Procedure

For advice on sampling see reference 5.

Read Section 4 on Hazards before starting this procedure

Step	Procedure	Notes
A7.1	**Liquid sludges** Mix the sample well and subsequently homogenize. If the dry solids content of the sample is known (note a), weigh into a dry 100 ml round bottom flask a quantity of sample which, when dry, will yield 1.0 ± 0.01 g dry solids. Dry the flask plus sample at 105 ± 2°C until no visible moisture is present. Allow the flask to cool to room temperature and proceed to step A7.4.	(a) If the dry solids content of the sample is not known, either determine the dry solids content and continue with step A7.1 or proceed to step A7.2.
A7.2	**Solid and semi-solid sludges** Dry a representative sample to constant weight, at 105 ± 2°C. Mix the dried sample by hand grinding in a pestle and mortar so that a representative sub-sample can be taken. Accurately weigh 1.0 ± 0.01 g into a dry 100 ml round bottom flask. Proceed to step A7.4.	
A7.3	**Soils and sediments** Cone and quarter a representative portion of <2 mm air dried, sieved sample prepared as described in (5). Grind a representative sub-sample (at least 10 g) to <150 μm size in the mill, and accurately weigh 3.0 ± 0.03 g into a dry 100 ml round bottom flask. Proceed to step A7.4.	
A7.4	**Digestion procedure** For each gram of dry sample, add 7.5 ± 0.2 ml hydrochloric acid (d_{20} 1.10) and 2.5 ± 0.1 ml nitric acid (d_{20} 1.40). Swirl the contents (note b). Connect the reflux condenser and leave to digest at room temperature overnight (at least 16 hours).	(b) Carry out the blank determination in a different set of apparatus each time, as recommended in Section 6.

A7.5 Boil gently under reflux for 2 hours ± 10 mins. Allow to cool slowly to about room temperature. Rinse the condenser with 25 ± 5 ml 12.5% V/V nitric acid, the liquid being collected in the round bottom flask. Remove the condenser (note c).

(c) The digestion of soil samples containing much carbonate or organic matter can be facilitated by ignition of the sample at 450 ± 20°C prior to the addition of the digesting acids.

A7.6 Filter the contents of the flask through an acid-resistant (hardened, ashless) cellulose filter paper (note d) into a 100 ml calibrated flask. Rinse the filter and residue five times with a few millilitres of warm (about 50°C) 12.5% V/V nitric acid. Allow to cool, add 1.00 ± 0.01 ml of 10% potassium solution as an ionization suppressant, and dilute with 12.5% V/V nitric acid. Shake thoroughly to mix the solution and retain for the atomic absorption stage.

(d) Filter paper porosity 0.4 to 1.1 μm capable of retaining particles >2.7 μm and previously washed with 12.5% V/V nitric acid.

A7.7 Blank determination

A blank must be carried out with each batch of sludges and a separate blank for soils. Blank determinations must use the same batch of reagents and the same volumes as that used for the samples. Add the digesting acids to the flask as described in step A7.4 and carry out steps A7.5 and A7.6.

A7.8 Atomic absorption stage

Set up the atomic absorption spectrometer as detailed in the manufacturer's handbook (note e). A nitrous oxide/acetylene flame should be used to minimize interference effects on the determination of chromium, iron and manganese in digests of soils or sediments (note f).

(e) A wash solution of 12.5% V/V nitric acid should be aspirated after each aspiration of a calibration standard, blank or sample. Always wash out the burner and spray chamber with distilled water at the end of the run.

A7.8.1 Mercury is determined by Atomic Fluorescence Spectrophotometry, see Ref 43 for details.

A7.9 Wavelengths used

Cadmium	228.8 nm
Chromium	357.8 nm
Copper	324.7 nm
Iron	248.3 nm
Lead	217.0 nm
Manganese	279.5 nm
Nickel	232.0 nm
Zinc	213.9 nm
(note g)	

(f) If a nitrous oxide/acetylene flame is not available chromium, iron and manganese can be determined in sludge extracts only using an air/acetylene flame. When determining chromium in an air/acetylene flame, however, set the acetylene flow to produce a flame on the verge of luminosity. This does not give maximum sensitivity, but does minimize inter-element effects.

(g) For wavelengths for other metals see the appropriate specific booklets in this series.

A7.10 Background correction

Background correction is essential when determining elements at wavelengths below about 300 nm, ie for cadmium, iron, lead, manganese, nickel and zinc.

A7.11 Calibration standards

Calibration standards incorporating 100 mg/l potassium should be prepared by taking appropriate aliquots of the standard metal solutions described in Section A5.7 and diluting to volume with 12.5% V/V nitric acid. Suitable standards contain up to 2 mg/l cadmium and zinc and up to 10 mg/l of the other metals.

A7.12 Method of measurements

Aspirate the calibration standards, blanks and samples with an aspiration of 12.5% V/V nitric acid between each solution (note h). Record the results, corrected for background if necessary, as a concentration of each metal in each sample digest, blank and standard by reference to the calibration curve.

(h) Some digests may require further dilution with 12.5% V/V nitric acid containing 1000 mg/l potassium to bring their metal concentrations within the working range. The dilution factor must be allowed for when calculating the result (see Section A10).

A7.13 Calculation of results

The sample contains $\frac{100\ (W - B)}{M}$ mg/kg dry weight where W is the concentration as mg/l of metal in the digest, B is the concentration as mg/l of metal in the blank and M is the weight of dry sample used in grams.

A8 Optimization of Instrumental Conditions

Care must be taken when setting up the atomic absorption spectrophotometer otherwise adequate precision and accuracy will not be obtained. The burner head and spray chamber should be washed with distilled water at the end of each run.

A9 Checking the Linearity of the Calibration Curves

The linearity of the calibration curves should be checked by running at least five calibration standards for each metal on at least two independent occasions before applying this method to any samples (see step A7.11). The calibration curve is normally linear for the range given in Section A1.4. If the calibration curve departs from linearity, the range given in Section 1.4 should extend only to the highest concentration on the linear part of the curve. However, with many modern atomic absorption spectrophotometers curve correction facilities may be used to give a direct concentration read out.

A10 Change of Concentration Range of the Method

If the metal concentrations in the sample digest (step A7.4) exceed the highest standard of the appropriate calibration curve then the measurement should be made on a suitable aliquot V_1 ml diluted with 12.5% V/V nitric acid containing 1000 mg/l potassium to 100 ml. The dilution factor must be taken into account in the calculation of the result (step A7.13) by multiplying by $\frac{100}{V_1}$.

A11 Sources of Error

The attention which it is necessary to pay to sources of error depends on the accuracy required of the analytical results. The following sub-sections summarize the main sources of error.

A11.1 Sampling Errors

Improper sampling and faulty sample reduction are among the commonest causes of error in analyses especially of inhomogeneous materials. It should be remembered that soils and sludges are very heterogeneous materials. See the various specialized booklets on sampling in this series. If in doubt, take several separate samples to check homogenity. See also Ref 5.

A11.2 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of these metals or their compounds are handled. The technique and working conditions should be critically examined and any sources of contamination eliminated and minimized. In particular, it is desirable to reserve the digestion flasks and associated condensers solely for this method.

A11.3 Interfering Substances

See Section A3. The effect of possible interfering substances may be determined by analysing soil and sludge digests spiked with the metals concerned and various concentrations of the potential interfering substance.

A12 Analyses of Peats, Peaty Soils and Plants

Tests have shown that the foregoing method will analyse peats and peaty soils which have up to at least 95% loss on ignition. However care is necessary, as there may be a tendency to foam with the consequent risk of spillage. If such foaming makes the sample too difficult to analyse, prior ashing at 450°C is useful. Due to the attendant risk of loss during ignition and transfer of the ash to the flask the test data above may not apply, though comparative tests indicate that provided care is taken the results should be almost the same.

Less testing has been carried out on plant analysis but with care either of these procedures should prove satisfactory.

A13 Checking the Accuracy of Analytical Results

Once methods have been put into normal routine operation, many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of tests are possible (7) and they should be used as appropriate. As a minimum, however, it is suggested that 10 ml of a suitable standard solution of the metals in 12.5% V/V nitric acid should be digested, together with and in exactly the same manner as the samples (see step A7.4 onwards). The results obtained should be plotted on a quality control chart, which will facilitate detection of inadequate accuracy and also allow the standard deviation of routine analytical results to be determined. Also standard reference materials should be analysed at regular intervals. Standard reference materials suitable for use in geological and environmental analysis are detailed in Chapter 3 of ARAAS (8).

B Dissolution of Residues Insoluble in Hydrochloric-Nitric Acid

B1 Introduction

Occasionally, it is necessary to analyse insoluble residues from Method A. The usual procedure is given below. It is based on work at the Norwegian and British Geological Survey Laboratories (Ref 9). For test data see Refs 10–15, see also Ref 41.

B2 Elements mentioned as likely to be brought into solution

(Lithium), Sodium, Potassium, Rubidium, Cesium, Magnesium, Calcium, (Strontium) (Barium), Boron, Aluminium, Titanium, Silicon, Phosphate, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Copper, (Zinc), (Germanium), Tin, Lead, (Zirconium), (Thorium) and (Arsenic).

Less information is given in the original papers on the elements in brackets. It is probable that the above list is not exhaustive.

B3 Outline

The sample is reacted with hydrofluoric acid which forms fluorosilicic acid and metal fluorides. Excess hydrofluoric acid is removed by reaction with boric acid to form fluoroboric acid. If required, silicon can be determined directly on this solution using one of the methods published in this series (Ref 16). Other metals can either be determined directly or after conversion to sulphate by fuming with sulphuric acid.

B4 Hazard

Hydrofluoric acid can produce severe skin burns associated with toxic symptoms which may not be noticed immediately due to a local anaesthetic effect hydrofluoric acid sometimes has on skin. **Use gloves and eye protection.** To prevent accidental burns due to small holes or other faults, gloves should be leak tested immediately prior to use. The wearing of two pairs of surgical grade gloves, one over the other is recommended. **Wash off even suspect splashes at once.** Careful methodical handling of equipment is the best protection. Always pour out hydrofluoric acid away from the label; always restopper and rinse the pouring side of the bottle after use and never handle bottles by that side; place stoppers and contaminated equipment where they cannot be touched accidently. **Measure out acid inside a shallow plastic tray. Rinse all contaminated apparatus clean immediately after use.** Be familiar with the first aid procedure and in the event of a burn, tell the doctor that hydrofluoric acid was in use. Do not distract technicians using this reagent. **Careful, unflustered technicians in many laboratories have used this procedure for many years without accident.**

For first aid advice see books recommended in Warning to Users.

B5 Reagents

B5.1 Water

B5.2 38–40% w/v Hydrofluoric Acid

B5.3 Boric acid, saturated solution

B5.4 Sulphuric Acid (d_{20} 1.84)

may also be required for some samples

B6 Apparatus

B6.1 A polytetrafluorethylene (PTFE) pot with a water tight but easily removed PTFE cap

B6.2 An aluminium pressure case with screw cap to contain the PTFE pot and cap

(with packing if necessary) such that the case cap holds the PTFE pot cap firmly closed when screwed down. The Parr general purpose acid digestion bombs (Parr Instrument Company, Moline, Illinois, USA) have been found suitable.

B6.3 An oven

thermostatically controlled for temperatures from 105–150°C.

B6.4 5 ml plastic measuring cylinder

B6.5 50-ml bulb pipette

B6.6 100-ml calibrated flask and stopper

B7 Analytical Procedure

READ THE HAZARD SECTION (B4 above) before starting this procedure.

Step	Procedure	Notes
B7.1	Filter off any insoluble residue from the hydrochloric-nitric acid digestion using a fine, acid washed hardened filter paper. Wash with a small portion of water to remove excess acid, combining washings and filtrate. Use the filtrate in the normal procedure above (note a).	(a) See step A7.6 in the preceding method.
B7.2	Carefully dry the filter paper at 105 ± 5°C and transfer all the insoluble material to the PTFE pot (B4.1). Add 5 ml of 38–40% w/v hydrofluoric acid, close the pot, place in its aluminium case, add any necessary packing and screw the cap onto the case (notes b and c).	(b) As soon as the hydrofluoric acid has been added to the samples wash out the measure and the reagent bottle outer surface (see Section B4). (c) The maximum amount of residue must not exceed 5 g. If necessary, weigh the total residue and use a representative weighed portion.
B7.3	Set the oven to 140–150°C, put the pot and case inside, allow to come up to a temperature and leave at temperature for 30 ± 5 minutes (note d).	(d) Some samples dissolve at much milder conditions. If experience shows this to be true, use a 105–110°C or other appropriate setting for the oven.
B7.4	Remove the container and PTFE pot from the oven and allow to cool to room temperature. Carefully remove the outer cap and packing. Open the PTFE pot (notes e and f).	(e) If there is undissolved residue reseal and reheat at 150°C for a further half hour. Cool as before and proceed. If there is still undissolved residue, consider an alternative method of analysis such as X-ray fluorescence spectroscopy (18, 19), or see note g. (f) There may be a precipitate present which is definitey not undissolved residue. If so, proceed to step B7.6.
B7.5	If the solution is clear, or the remaining undissolved solid is negligible, add 50.0 ± 0.2 ml of saturated boric acid solution. Proceed to step B7.7.	(g) If it is suspected that the residue is an insoluble fluoride, it may be possible to dissolve it by fuming with sulphuric, phosphoric or perchloric acids, the choice depending on the solubility of the sulphates and acid phosphates of the main and sought metals likely to be present (see Ref 41).
B7.6	If there is precipitate present, but not undissolved sample requiring a longer or hotter digestion, add 50±0.2 ml of saturated boric acid solution, close the PTFE pot and container as before and heat in the oven at 105–110°C for 30 ± 5 minutes. Cool and open the pot as before (note g).	
B7.7	Transfer the digest quantitatively to a 100 ml calibrated flask using small portions of rinse water. Make up to the mark with water, and mix.	

Step	Procedure	Notes
B7.8	Use this solution for analysis as required (note h).	(h) If interference is suspected from fluoroborate, prepare a set of compensated standard samples as follows: for each standard add 5 ml hydrofluoric acid to 50 ml of saturated boric acid in a plastic beaker, transfer quantitatively to a 100 ml calibrated flask, add the requisite amount of the necessary standard concentrated solution and make up to the mark with water. If necessary, fluoroboric acid can be removed by fuming samples with sulphuric, phosphoric or perchloric acids, the choice is dependent on the solubility of the sulphates and acid-phosphates of the main and sought metals likely to be present. (For a variant see Ref 17.)

C The Determination of Acid Soluble Aluminium, Cadmium, Calcium, Chromium, Cobalt, Copper, Iron, Lead, Magnesium, Manganese, Molybdenum, Nickel, Silver and Zinc in Sewage Sludges by Atomic Absorption Spectrophotometry following Digestion with a Hydrochloric and Nitric Acid Mixture

Note:
(1) Throughout this method, aluminium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, silver and zinc are expressed as their respective elements Al, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Ag and Zn.
(2) This method is similar to a previously published method in this series (4), but is applicable to a wider range of elements.

C1 Performance Characteristics of the Method

C1.1	Substances determined	Al, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, Ag and Zn. Arsenic and Mercury may also be determined on this digest (35, 36, 40).	
C1.2	Type of sample	Sewage Sludge (dried at 105°C).	
C1.3	Basis of method	Digestion with hydrochloric acid and nitric acid (3:1) in a 50 ml calibrated tube, measurement of metal concentration by atomic absorption spectrophotometry in either an air-acetylene or a nitrous oxide-acetylene flame.	
C1.4	Range of application (without dilution of digest or rotation of the burner)	Al	30–10,000 mg/kg dry weight
		Cd	0.8–100 mg/kg dry weight
		Ca	1,500–150,000 mg/kg dry weight
		Cr	2–500 mg/kg dry weight
		Co	3–500 mg/kg dry weight
		Cu	1–500 mg/kg dry weight
		Fe	50–20,000 mg/kg dry weight
		Pb	6–500 mg/kg dry weight
		Mg	40–3,000 mg/kg dry weight
		Mn	6–1,000 mg/kg dry weight
		Mo	5–500 mg/kg dry weight
		Ni	5–500 mg/kg dry weight
		Ag	2–250 mg/kg dry weight
		Zn	10–250 mg/kg dry weight
C1.5	Calibration curve	Almost linear over the concentration ranges given in Section C1.4.	

C1.6 Total standard deviation (expressed as mg/kg) (dried weight)

	Metal	Concentration of metal (mg/kg)	Total standard deviation (mg/kg)	R.S.D (%)
Sludge 1 – from a works serving a highly industrial area	Al	8187	288.5	3.52
	Cd	35.9	0.51	1.43
	Ca	52550	737	1.40
	Cr	3341	55.8	1.67
	Co	55.7	1.62	2.91
	Cu	6756	76.6	1.13
	Fe	36840	4295	11.7
	Pb	609	17.2	2.83
	Mg	3741	59.7	1.60
	Mn	767	5.97	0.78
	Mo	128	4.27	3.33
	Ni	1852	14.3	0.77
	Ag	40.9	0.79	1.92
	Zn	1855	64.2	3.46
Sludge 2 – from works receiving little trade effluent	Al	3231	84.3	2.61
	Cd	3.27	0.23	6.92
	Ca	28510	346	1.22
	Cr	42.2	2.39	5.68*
	Co	3.96	0.97	24.5
	Cu	274	4.38	1.60
	Fe	6898	280	4.39
	Pb	281	3.09	1.10
	Mg	3286	83.7	2.55
	Mn	284	5.00	1.76*
	Mo	3.02	0.91	30.3
	Ni	22.8	1.45	6.37
	Ag	6.32	0.60	9.43
	Zn	608	37.8	6.21
Sludge 3 – Certified Reference Material BCR No. 144 (results obtained over a 12-week period)	Cd	3.54 (3.41)	0.232	6.55
	Cr	453 —	16.4	3.62
	Cu	697 (713)	35.1	5.04
	Ni	961 (942)	28.1	2.92
	Pb	460 —	21.1	4.59
	Zn	3107 (3143)	70.1	2.26

Figures in brackets are certified values.

Except for the two results marked (*) which were with 8 degrees of freedom all the above data has 9 degrees of freedom.

C1.7 Limit of detection (expressed as mg/kg dry (weight)

The following results were calculated from within a batch standard deviation of 10 replicate blank measurements assuming a 0.5 g sample of dried sludge.

Metal	Limit of detection (mg/kg)
Al	28
Cd	0.8
Ca	1440
Cr	2
Co	3
Cu	1
Fe	47
Pb	6
Mg	37
Mn	6
Mo	5
Ni	5
Ag	2
Zn	10

C1.8 Sensitivity

Metal	Concentration (mg/kg)	Absorbance
*Al	2500	0.300
Cd	100	0.440
*Ca	40000	0.140
*Cr	100	0.100
Co	100	0.120
Cu	100	0.200
*Fe	5000	0.340
Pb	100	0.080
*Mn	200	0.190
*Mo	100	0.050
Ni	100	0.150
Ag	100	0.200
Zn	50	0.400

* Using a nitrous oxide/acetylene flame; other values using an air/acetylene flame.

C1.9 Bias. Not thought to be significant (see Section C3).

C1.10 Interferences. See Section C3.

C1.11 Time Required for Analysis.

Starting with dried (105°C) sludge – unground and unsieved, the times required for 14 elements in 30 samples and the associated calibration standards are given below:

Sample Preparation	3 hours
Digestion	1.5 hours
Filtration	0.5 hours
Measurement	9 hours

The above data were obtained by Yorkshire Water Authority, Sheffield.

C2 Principle

0.5 g of dried sludge is digested with 6 ml of hydrochloric acid (d_{20} 1.18) and 2 ml of nitric acid (d_{20} 1.42) in a 50 ml calibrated borosilicate glass boiling tube. After the digestion is completed caesium chloride and ammonium perchlorate are added to the digests to minimize any interference effects. After dilution to 50 ml and filtration, the metals are determined by atomic absorption spectrophotometry using air-acetylene or nitrous oxide-acetylene flames.

C3 Interferences

Interference effects in complex matrices such as sludge digests are dependent upon the instrument and flame conditions used.

C3.1 Chemical interference effects are minimized by the addition of 1% m/V ammonium perchlorate to all sample digests, blanks and standards. Without the ammonium perchlorate addition low molybdenum results are observed.

C3.2 The nitrous oxide acetylene flame is used to determine Al, Ca, Fe, Mg, Mn and Mo. The latter elements are prone to chemical interference effects when determined in the air-acetylene flame. Caesium chloride is added as an ionization suppressant.

C3.3 Results for Cd, Cu, Ni and Zn using a certified reference sludge indicates that the method is satisfactory for these elements. In addition previous work (4, 21) carried out with nitric acid digests indicates that chemical interference effects were not significant for Cd, Cu, Ni, Pb and Zn in the air-acetylene flame.

C4 Hazards

Digestions with aqua regia are potentially hazardous. The calibrated tubes should be positioned on the heating mantles, in a well-ventilated fume cupboard, shielded from the operator. It is essential to add anti-bumping granules to prevent bumping. The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away.

C5 Reagents

Analytical grade reagents are suitable unless otherwise specified. All reagents and standard solutions should be stored in polyethylene bottles unless otherwise specified.

C5.1 Water

The water used for the blank determinations and for preparing the reagents and standard solutions should have metal contents that are negligible compared with the smallest concentrations of the metals to be determined in samples. Water distilled from an all glass apparatus or dionized water is suitable.

C5.2 Nitric acid (d_{20} 1.42)

C5.3 Hydrochloric acid (d_{20} 1.18)

If sufficiently pure acid is not available, see method A, but take steps to re-saturate with HCl.

C5.4 Aluminium oxide anti-bumping granules

These should be soaked in 10% V/V nitric acid overnight, washed thoroughly in water, dried and stored in a dry bottle.

C5.5 Standard metal solutions

Commercially available 1,000 mg/l standards, diluted appropriately to produce working standard solutions are satisfactory.

C5.6 Ammonium perchlorate solution 10% m/V (high purity)

This is available from BDH Chemicals Ltd.

C5.7 Caesium chloride (50,000 mgl^{-1})

Dissolve 63.35 g ± 0.1 g of caesium chloride, dried for 1 hour at 105°C, in 500 ± 100 ml of water, dilute to 1 litre in a volumetric flask.

C5.8 Dodecane (General purpose reagent)

C6 Apparatus

C6.1 An atomic absorption spectrophotometer

equipped for both nitrous oxide and air-acetylene flames, with suitable hollow cathode lamps.

Background correction will be required for elements determined at wavelengths less than 300 mm (see section C9.7). A general guide to the use of atomic absorption spectrophometry is given in reference (21).

C6.2 10-ml capacity calibrated glass/PTFE Winchester dispenser

Suitable for dispensing both nitric and hydrochloric acids. The dispensers should be set to 2.0 ± 0.1 ml and 6.0 ± 0.1 ml respectively.

C6.3 50-ml calibrated borosilicate glass tubes

Internal diameter approximately 23 mm and fitted with ground glass or polyethene stoppers.

C6.4 Heating apparatus

The digestion is carried out in a micro Kjeldahl digestion apparatus. This comprises a rack of six heating mantles suitable for 20–50 ml capacity round bottom flasks. Each mantle has its own temperature controller. Each flask is so supported that it points at the wall.

C7 Sample Collection and Preservation

No special sample collection or preservation techniques are normally required. A clean 2 litre plastic container with a wide mouth is suitable. The main problem is to obtain a representative sample (see another publication in this series (5)). In order to minimize bacterial activity the samples should be stored at approximately 4°C with the tops of the containers slightly loosened to facilitate the escape of any gas which may form.

C8 Determination of the Percentage Dry Solids and Preparation of the Dried Sludges

The percentage of dry solids in wet sludge should be determined by drying a suitable aliquot at 105 ± 2°C to constant weight. The dried sludge should be ground with a glass pestle and mortar and passed through a 2 mm mesh aluminium or stainless steel sieve. For samples expected to be low in metal content use of a nylon or similar metal free plastic sieve may be advisable.

C9 Analytical Procedure

Step	Procedure	Notes
	Digestion Procedure	
C9.1	Transfer 0.500 ± 0.002 g of the ground dried sludge into a 50 ml calibrated borosilicate tube. Run 1.0 ± 0.1 ml of water down the side of the tube to wet the sample. Add 3 or 4 aluminium oxide anti-bumping granules.	
C9.2	Carefully run 6.0 ± 0.1 ml of hydrochloric acid (d_{20} 1.18) and 2.0 ± 0.1 ml of nitric acid (d_{20} 1.42) down the side of the tube. Place the tube in a rack and allow any vigorous initial reaction to subside. If excessive foaming occurs add 2 drops of n-dodecane. Place the tube on the heating mantle and adjust the heating control until the sample gently refluxes.	
C9.3	Allow the sample to reflux for 10 ± 2 minutes. Run 5.0 ± 0.1 ml water down the side of the tube and reflux for a further 5 ± 1 minute.	

Step	Procedure	Notes
C9.4	Allow the tube to cool. Add 1 ± 0.02 ml of 50,000 mgl^{-1} Cs solution and 5 ± 0.1 ml of 10% w/v ammonium perchlorate solution. Dilute with water to 50 ml. Replace the ground glass stopper, shake vigorously and filter through an acid resistant (hardened ashless) cellulose filter paper (note a) into a polypropylene bottle.	(a) Filter paper porosity 0.4–1.1 μm capable of retaining particles greater than 2.7 μm and previously washed with 10% V/V nitric acid.
	Blank Determination	
C9.5	Two blanks should be run with each batch of determinations. Add 1.0 ± 0.1 ml of water and then proceed under sections C9.2 to C9.4. Note (b).	(b) Carry out the blank determination in different tubes each time.
	Calibration Standards	
C9.6	Multielement calibration standards of suitable concentration should be prepared in 6% V/V hydrochloric acid – 2% V/V nitric acid containing 1,000 mgl^{-1} Cs and 1% m/V ammonium perchlorate. The chromium must be in the (III) valent state. Standards containing 2 mgl^{-1} or less should be prepared weekly; standards containing greater than 2 mgl^{-1} are stable for at least one month.	
	Background Correction	
C9.7	Background correction is essential when determining elements at less than 300 nm (see section C9.9).	
	Atomic Absorption Stage:	
C9.8	Set up the atomic absorption spectrophotometer as detailed in the manufacturer's handbook. Note (c).	(c) A wash solution of 1% V/V nitric acid should be aspirated after each aspiration of a calibration standard, blank or sample.
	Wavelengths and Flames Used	

C9.9

Element	Wavelength	Flame
Aluminium	309.3 nm	N
Cadmium	228.8 nm	A
Calcium	430.7 nm	N
Chromium	357.9 nm	N
Cobalt	240.7 nm	A
Copper	324.7 nm	A
Iron	372.0 nm	N
Lead	217.0 nm	A
Magnesium	202.5 nm	N
Manganese	279.5 nm	N
Molybdenum	313.3 nm	N
Nickel	232.0 nm	A
Silver	328.1 nm	A
Zinc	213.9 nm	A

Note: A = Air-acetylene
N = Nitrous oxide-acetylene

Step	Procedure	Notes
	Method of measurement	
C9.10	Insert the nebulizer capillary into the filtered sample solution. Record the result, corrected for background if necessary (see step C9.7), as a concentration for each metal in each sample digest, blank and standard (by reference to the calibration curve). Note (d).	(d) Some digests may require dilution with a solution containing 6% V/V hydrochloric acid – 2% V/V nitric acid – 1% m/V ammonium perchlorate and 1000 mg/l caesium. The dilution factor must be allowed for when calculating the result.
	Calculation of results	
C9.11	The sample contains 100 (W-B) mg/kg dry weight where W is the concentration of metal in the digest and B is the concentration of metal in the blank.	

C10 Optimization of Instrumental Conditions

Care must be taken when setting up the atomic absorption spectrophotometer otherwise adequate precision and accuracy will not be obtained (6). The burner head and spray chamber should be washed with hot water at the end of each run.

C11 Checking the Linearity of the Calibration Curves

The linearity of the calibration curves should be checked by running standards on at least two independent occasions before applying this method to any samples. The calibration curve is almost linear for the range given in Section C1.4. If the calibration curve departs significantly from linearity, the range given in Section C1.4 should be reduced. However, with modern atomic absorption spectrophotometers curve correction facilities may be used to give a direct concentration read out.

C12 Changing the Concentration Range of the Method

If the metal concentrations in the sample digest (Step C9.4) exceed the highest standard of the appropriate calibration curve then the measurement should be made on a suitable aliquot V_1 ml, diluted to 50 ml with 6% V/V hydrochloric acid, 2% V/V nitric acid, 1% m/V ammonium perchlorate and 1,000 mg/l Cs. The dilution factor must be taken into account in the calculation of the result (Steps C9.10 and C9.11) by multiplying by $50/V_1$.

C13 Sources of Error

The attention which it is necessary to pay sources of error depends on the accuracy required of the analytical results. The following sub-sections summarize the main source of error.

C13.1 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of these metals or their compounds are handled. The technique and working conditions should be critically examined and any sources of contamination eliminated or minimized. In particular, it is desirable to reserve the 10 ml and 50 ml glass tubes solely for this method.

C13.2 Interfering Substances – see Section C3.

C14 Checking the Accuracy of Analytical Results

Once methods have been put into normal routine operation, many factors may subsequently, adversely affect the accuracy of the analytical results. It is recommended that experimental tests, to check certain sources of inaccuracy, should be made regularly. Many types of tests are possible (7) and they should be used as appropriate. As a minimum, however, it is suggested that 10 ml of a suitable standard solution of the metals in 6% V/V hydrochloric acid, 2% V/V nitric acid should be digested, together with, and in exactly the same manner as, the samples. The results obtained should be plotted on a quality control chart, which will facilitate detection of inadequate accuracy and also allow the standard deviation of routine analytical results to be determined. Another means of estimating the accuracy of the method is to analyse a Certified Reference Material and plot this data on a quality control chart.

D The Determination of Acid Soluble Cadmium, Chromium, Copper, Lead, Manganese, Nickel and Zinc in Soils by Atomic Absorption Spectrophotometry following Digestion with a Hydrochloric and Nitric Acid Mixture

Note: Throughout this method cadmium, chromium, copper, lead, manganese, nickel and zinc are expressed as their respective elements Cd, Cr, Cu, Pb, Mn, Ni and Zn.

D1 Performance Characteristics of the Method

D1.1	Substances determined	Cd, Cr, Cu, Pb, Mn, Ni and Zn.
D1.2	Type of sample	Soil.
D1.3	Basis of method	A sample of air-dried sieved and ground soil is digested under reflux with aqua regia for 2 hours. The metals are then determined by atomic absorption spectrophotometry (AAS).
D1.4	Range of application (without dilution of digest or rotation of the burner)	Cd 0.2 – 20 Cr 0.8 – 100 Cu 0.6 – 100 Pb 1 – 100 Mn 1.3 – 100 Ni 0.6 – 100 Zn 0.2 – 50
D1.5	Calibration curve	Amost linear over the concentration ranges given in Section D1.4.

D1.6 Within batch standard deviation (expressed as mg/kg dried weight)

	Metal	Concentration of metal mg/kg		Within batch standard deviation (mg/kg)		RSD %		Degrees of freedom	
		1*	2*	1	2	1	2	1	2
Soil 1. A calcareous uncontaminated loam soil. Certified Reference Material CRM 141.	Cd	0.32	0.29	0.017	0.012	5.3	4.0	4	3
	Cr	52.4	48.4	0.78	0.53	1.5	1.1	4	3
	Cu	25.3	30.8	0.50	0.91	2.0	3.0	4	3
	Mn	511	503	5.4	2.6	1.1	0.51	4	3
	Ni	25.4	24.6	0.26	0.53	1.0	2.1	4	3
	Pb	21.1	22.5	0.54	0.44	2.6	2.0	4	3
	Zn	65.5	68.4	0.76	1.43	1.2	2.1	4	3

* 1 and 2 refer to two separate batches.

The 'total' and aqua regia soluble certificate values for the above elements together with their standard deviations are given below:

Element	Certificate Values (and Standard Deviations) mg/kg for CRM 141			
	Total (Certified results)		Aqua Regia Soluble	
Cd	0.36	(0.10*)	0.30	(0.13)
Cr	75	(10.4)	53	(9)
Cu	32.6	(1.4*)	31.2	(2.3)
Mn	547	(32)	512	(63)
Ni	30.9	(3.2)	28	(4.9)
Pb	29.4	(2.6*)	26.3	(5.3)
Zn	81.3	(3.7*)	70	(11)

* 95% confidence limit

D1.7 Limit of detection (expressed as mg/kg dry weight)

The following results were calculated from the within batch standard deviation of 10 replicate blank measurements assuming a 2.5 g sample of soil:

Metal	Limit of detection mg/kg
Cd	0.2
Cr	0.8
Cu	0.6
Pb	1.0
Mn	1.3
Ni	0.6
Zn	0.2

D1.8 Sensitivity

	Metal	Concentration Absorbance (mg/kg)
Cd	20	0.44
*Cr	20	0.10
Cu	20	0.20
Pb	20	0.08
*Mn	40	0.19
Ni	20	0.04
Zn	10	0.40

* Nitrous/acetylene flame.

D1.9 Bias

See Section D3.

D1.10 Interferences

See Section D3.

D1.11 Time required for analysis

Starting with dried, unground and unsieved material.

The times required for 7 elements in 12 samples are as follows:

Sample preparation	2.5 hours
Digestion	2 hours
Filtration	0.5 hours
Measurement	2.0 hours

The above data were obtained by Yorkshire Water Authority, Sheffield.

D2 Principle

D2.1 A 2.5g aliquot of air-dried soil is digested with aqua regia. After digestion is completed caesium chloride is added to the digests. After dilution to 50 ml and filtration the metals are determined by atomic absorption spectrophotometry.

D2.2 The metal contents of soils are required for monitoring sludge disposal and to decide upon the rates of sludge disposal on agricultural land. The method does not determine the total metal content but some 70 to 90 per cent of the total contents of Cd, Cr, Cu, Mn, Ni, Pb and Zn are extracted from uncontaminated topsoils and an even greater proportion from sludge-contaminated soils. The aqua regia insoluble metal is not thought to be toxicologically significant.

D3.1 Interference effects in complex matrices such as soil digests are dependent upon the instrument and flame conditions used.

D3.2 Chemical interference effects for Cd, Cu, Ni, Pb and Zn in the air acetylene flame are not thought to be significant if a slightly fuel lean flame is used and the burner height set 2–3 mm below grazing incidence.

D3.3 The nitrous oxide-acetylene flame is used to determine Cr and Mn. Caesium chloride is added as an ionization suppressant.

D3.4 If it is necessary to determine molybdenum, 1% m/V ammonium perchlorate should be added to all samples, standards and blanks. This was found to overcome the interference effect of calcium upon molybdenum.

D3.5 Results for Cd, Cr, Cu, Mn, Ni, Pb and Zn using a certified reference soil indicates that the method is satisfactory for these elements (see Section D1.5).

D4 Hazards

See Section C4.

D5 Reagents

Analytical grade reagents are suitable unless otherwise specified. All reagents and standard solutions should be stored in polyethylene bottles unless otherwise specified.

For details see the corresponding reagents in Section C5.

D6 Apparatus

D6.1 An atomic absorption spectrophotometer

equipped with both air-acetylene and nitrous oxide-acetylene flames and suitable hollow cathode lamps. Background correction will be required for elements determined at wavelengths less than 300 nm (See Section D9.7). A general guide to the use of atomic absorption spectrophotometry is given in reference(6).

D6.2 10 and 20 ml capacity calibrated glass/PTFE Winchester dispensers

suitable for dispensing nitric and hydrochloric acid. The dispensers should be set to 4.0± 0.1 ml for the nitric acid and 12.0± 0.1 ml for the hydrochloric acid.

D6.3 100 ml calibrated borosilicate glass tubes

(190 mm length, 35 mm o.d.) with a B29/22 ground glass socket fitted with air condenser tubes (145 mm length, 29 mm o.d.) with a B29/22 ground glass cone. The tubes should be fitted with ground glass or polyethylene stoppers.

D6.4 Heating apparatus

See Section C6.4.

D6.5 Ball Mill or Grinder

This should be capable of reducing the particle size of the soils to less than 150 μm.

D7 Sample Collection and Preservation

No special sample collection or preservation techniques are required. A clean 2 litre plastic container with a wide mouth or a stout polythene bag. The main problem is to obtain a representative sample (see another publication in this series(5).

D8 Preparation of the Soil for Analysis

Cone and quarter a representative portion of the less than 2 mm air dried, sieved sample as described in ref (5). Grind a representative sub-sample (at least 10 g) to less than 150 μm in a suitable mill.

D9 Analytical Procedure

Step	Procedures	Notes
D9.1	Transfer 2.5 ± 0.005 g of the ground soil into a 100 ml digestion tube fitted with a small air condenser.	
D9.2	Wet the sample by adding 5± 0.5 ml of water.	
D9.3	Carefully run 12± 0.2 ml of hydrochloric acid (d_{20} 1.18) and 4 ml± 0.1 ml of nitric acid (d_{20} 1.42) down the side of the tube. Place the tube in a rack and allow any vigorous initial reaction to subside.	
D9.4	Add 1± 0.05 ml n-dodecane and a few anti-bumping granules.	
D9.5	Place the tube on the heating mantle and adjust the heating control until the sample gently refluxes. (Note a).	(a) For some soils the heating control must be increased slowly to prevent excessive foaming and loss of tubes contents.
D9.6	Digest for 2 hours under gentle reflux.	
D9.7	Allow the tube to cool. Add 1 ± 0.02 ml of 50,000 mgl^{-1} caesium solution and dilute to 50 ml with distilled water.	
D9.8	Mix thoroughly and filter through an acid resistant (hardened ashless) cellulose filter paper (note b) into a polypropylene bottle.	(b) Filter paper porosity 0.4 – capable of retaining particles greater than 2.7 μm and previously washed with 10% V/V nitric acid.
	Blank Determination	
D9.9	Two blanks should be run with each batch of determinations. Add 5.0± 0.5 ml of water and then proceed under sections 9.3 to 9.8. Note (c).	(c) Carry out the blank determinations in different tubes each time.
	Calibration Standards	
D9.10	Multielement calibration standards of suitable concentration should be prepared in 12% V/V hydrochloric acid – 4% V/V nitric acid containing 1,000 mgl^{-1} Cs. The chromium must be in the (III) valent state. Standards containing 2 mg/l or less should be prepared weekly; standards containing greater than 2 mg/l are stable for at least one month.	
	Background Correction	
D9.11	Background correction is essential when determining elements at less than 300 nm (See Section 9.13).	

Atomic Absorption Stage:

D9.12 Set up the atomic absorption spectrophotometer as detailed in the manufacturer's handbook. Note (d).

(d) A wash solution of 1% V/V nitric acid should be aspirated after each aspiration of a calibration standard, blank or sample.

Wavelengths and Flames Used:

D9.13

Element	Wavelength	Flame
Cadmium	228.8 nm	
Chromium	357.9 nm	N
Copper	324.7 nm	A
Lead	217.0 nm	A
Manganese	279.5 nm	N
Nickel	232.0 nm	A
Zinc	213.9 nm	A

Note: A = Air-acetylene.
N = Nitrous oxide-acetylene.

Method of Measurement

D9.14 Insert the nebulizer capillary into the filtered sample solution. Record the result, corrected for background if necessary (see Step 9.11), as a concentration for each metal in each sample digest, blank and standard (by reference to the calibration curve). Note (e).

(e) Some digests may require dilution with a solution containing 12% V/V hydrochloric acid – 4% V/V nitric acid and 1,000 mg/l caesium. The dilution factor must be allowed for when calculating the result.

Calculation of Results

D9.15 The sample contains 20 (W-B) mg/kg dry weight where W is the concentration of metal in the digest and B is the concentration of metal in the blank.

D10 Optimization of Instrumental Conditions

See Section C10.

D11 Checking the Linearity of the Calibration Curves

See Section C10, reading D1.4 for C1.4.

D12 Changing the Concentration Range of the Method

If the metal concentrations in the sample digest (Step D9.8) exceed the highest standard of the appropriate calibration curve then the measurement should be made on a suitable aliquot V_1 ml, diluted to 50 ml with 12% V/V hydrochloric acid 4% nitric acid and 1,000 mg/l Cs. The dilution factor must be taken into account in the calculation of the result (steps D9.14 and D9.15 by multiplying by $50/V_1$).

D13 Source of Error

See Section C13.

D14 Checking the Accuracy of Analytical Results

Once methods have been put into normal routine operation, many factors may subsequently, adversely affect the accuracy of the analytical results. It is recommended that experimental tests, to check certain sources of inaccuracy, should be made regularly. Many types of tests are possible and they should be used as appropriate. As a minimum, however, it is suggested that 5 ml of a suitable standard solution of the metals in 12% V/V hydrochloric acid, 4% V/V nitric acid should be digested, together with, and in exactly the same manner as, the samples. The results obtained should be plotted on a quality control chart, which will facilitate detection of inadequate accuracy and also allow the standard deviation of routine analytical results to be determined. Another (better) means of estimating the accuracy of the method is to analyse a Certified Reference Material and plot this data on a quality control chart.

E Estimation of the Accuracy of Analytical Results for Variants of the Methods Given

(The Standing Committee would be grateful if laboratories investigating variants on these methods would copy their findings to the address given below for correspondence)

E1 Introduction

Before putting a variant of this method into general use, it is desirable to know the accuracy achievable in the laboratory.

The accuracy and practicable range achieved and the effects of any interfering substances that may be present in samples are of particular interest. Suggestions for a suitable experimental design and analysis of results are given in the following sections. The design has been chosen to be as simple as possible; more complex designs are possible and would give more information. (See also ref 7).

E2 Basis of Suggested Tests

The limit of detection is governed by the within-batch variability of blank determinations. The precision of analytical results may depend on the concentration of determinand in the sample analysed and on the type of sample, worse precision may be obtained with real samples than with standard solutions. For these reasons the basic design recommended is the analysis of one portion of each of the following samples on each of n days, where n is at least 5 and preferably up to 10.

Information on the probable range of the method can be obtained by comparing with the specific method published in this series.

Sample No	Description
1	Blank
2	Another blank
3	A sample free of determinand metal
4	A repeat of sample 3
5	Sample 3 spiked with the metal at between two and five times the expected limit of detection
6	Sample 3 spiked with the metal to about the upper middle of the expected range of the method
7	Typical sample
8	Sample 7 spiked with 10.0 µg/l metal or other suitable known amount

It is essential that these samples be treated exactly as if they were samples and the procedure specified in the method be rigidly followed. These samples should be analysed in random order in each batch of analyses. The total period of the tests may be any convenient time so long as the determinand metal concentration does not change appreciably (up to 2 weeks). The results of the analyses of solutions 3 and 8 will provide a check on the effect of sample type on precision. Any deviation of the recovery of spike from 100% may give an indication of the presence of interfering substances.

E3 Evaluation of Results

E3.1 Convert all results to concentrations as described in the method. Deduct the first of the two blank values from each of the other values.

E3.2 Calculate the mean concentration of the n results for each sample.

E3.3 Calculate the standard deviation, s, of the n results for each sample from:

$$s = \frac{\sum(X_i - X)^2}{n - 1}$$

where X_i = the result from the ith batch
X = the mean value of X_i.

E3.4 Calculate the within-batch standard deviation, s_w, of the blank from:

$$s_w = \frac{\sum(X_{1i} - X_{2i})^2}{2n}$$

where X_{1i} = the 1st blank result from the ith batch
X_{2i} = the 2nd blank result from the ith batch.

E3.5 Calculate the mean percentage recovery, R, of the spiked sample 8:

$$R = \frac{(X_8 - X_7)}{D} \times 100$$

where X_7 = the mean value of the results for sample 7
X_8 = the mean value of the results for sample 8, and
D is the spike concentration for sample 8, usually 10μg/l.

E4 Detection of Interference

If interference is suspected, if possible, obtain a qualitative analysis of the sample by DC arc emission, ICP or preferably XRF spectrometric analysis. (see Refs 18 and 19). Look for elements with overlapping spectral lines or band spectra, elements with lower line excitation potentials, and elements which could react with the determinand to form substances with much lower or higher volatility than the determinand alone in the spectral method used. Ref 18 lists suitable compendia.

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Addendum to Chromium in Raw and Potable Waters and Sewage Effluents 1980

Method A in this 1980 booklet uses an Air-Acetylene burner with the Atomic Absorption Spectrophotometer (A6.1 and A9.11 to A9.16). However, not all instruments give reliable results for Chromium with this flame. Many laboratories have changed to Nitrous Oxide-Acetylene burners with an improvement in the performance characteristics.

Address for Correspondence

However thoroughly a method may be tested, there is always the possibility of a user discovering a hitherto unknown problem. Users with information on this method are requested to write to:

The Secretary
The Standing Committee of Analysts
The Department of the Environment
Romney House
43 Marsham Street
LONDON SW1P 3PY
England

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