

Extractable Metals in Soils, Sewage Sludge-treated Soils and Related Materials 1982

Methods for the Examination of Waters and Associated Materials

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Two methods are described; method A uses EDTA as the extractant; method B uses acetic acid as the extractant. Both methods use an atomic absorption spectrophotometric final determination.

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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. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. 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.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for 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 Series No. 6, HMSO, London.

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. 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 later case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

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. 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.

About this series

This booklet is one of a series intended to provide recommended methods for the determination of water quality. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, has 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 individual methods, 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 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 analytical chemist, biologist, bacteriologist etc. to decide which of these methods to use for the determination in hand. Whilst 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 one of the joint technical committees of the Department of the Environment and the National Water Council. It now has seven Working Groups, each responsible for one 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 etc. are produced by small 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.

T A DICK
Chairman

L R PITTWELL
Secretary

8 November 1982

The Determination of Extractable Metals in Soils, Sewage Sludge Treated Soils and Related Materials

General Introduction

1. The total content of trace elements in soils provides a general indication of their status and potential availability to plants but no information on their forms of occurrence. Trace elements may be present in the soil solution or held as readily exchangeable ions, as more firmly bound ions, as chelated ions, incorporated in precipitated oxides or insoluble salts and fixed in the crystal lattices of secondary or primary minerals. Water soluble and exchangeable ions are generally held to be readily available to plants but often represent only a very small proportion of the total content.

2. Some form of extraction is normally employed for the empirical assessment of the availability of soil constituents to the plant and an ideal extractant would simulate plant behaviour in so far as the uptake of all elements is concerned. Such an ideal extractant is not available. The varied forms of combination of different elements in the soil and the fact that plant contents of trace elements vary depending upon species, the part of the plant sampled and seasonal changes during growth are all factors which have to be considered in relating the trace element content of soil extracts to plant uptake. The extractant used must be both analytically convenient and diagnostically acceptable and will depend on the nature of the soil and the properties of the element in question.

3. For much investigational work a dilute acid extractant is used to assess the availability to plants of elements such as cobalt, nickel and zinc present in soils in exchangeable cation form. Some trace elements occur in soils as metal-organic complexes that appear to be available to plants and for copper it has been found that ethylene diamine tetra-acetic acid (EDTA) provides a more satisfactory diagnostic correlation with plant uptake or response to added copper than does a dilute acid extractant.

4. In a cool, temperate climate such as that in Britain arable topsoils are generally acid and often require liming to about pH 6 – 6.5 for good crop growth. Thus for many soils in Britain acetic acid has been found to be a suitable extractant for available cobalt, nickel and zinc. For calcareous soils, however, a dilute acid extractant may be unsatisfactory as it may be neutralised by free lime present in the soil. In such cases a neutral extractant such as 0.05 M EDTA may therefore be preferable. The Agricultural Development and Advisory Service (ADAS) have recently adopted 0.05 M EDTA as a general extractant for readily available cadmium, copper, nickel and zinc in soils because all four elements, particularly in cases where pollution has arisen, can be determined directly by atomic absorption following a single extraction.

5. Solutions of 0.05 M EDTA and 0.5 M acetic acid are widely used in assessing the availability of a number of trace elements in soils and the methods for the determination of these are described in this booklet. Whichever extractant is employed it must be emphasised that it is necessary to establish experimentally the relationship between soil content and plant or animal behaviour under local conditions. All determinations of extractable trace metals described in this booklet are carried out on air-dried samples which have been ground through a 2mm-sieve⁽¹⁾.

6. Many cultivated surface soils, after air-drying and sieving have a density of around 1.0, notable exceptions being peats or soils with very high organic matter contents. With light peaty soils it may be useful therefore to express concentrations of metals on a m/V basis rather than a m/m basis to facilitate the interpretation of the amounts of elements available in the rooting zone of plants. For the majority of cultivated surface soils however differences between the two are probably small. It is recommended therefore that concentrations of metals in soils, sewage sludges and related materials be determined and expressed on a m/m basis. In those cases where it may be necessary to express levels on a m/V basis, a conversion factor can be applied, following determination of the density of the dry sample.

A. Cadmium, Copper, Lead, Manganese, Nickel and Zinc Extractable by 0.05M EDTA in Soils, Sewage Sludge Treated Soils and Related Materials

A1 Performance characteristics of the method

(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Results 1980, also published in this series.)

A1.1	Substances determined	Extractable cadmium, copper, lead, manganese, nickel and zinc.
A1.2	Type of sample	Soils, sewage sludge treated soils and related materials.
A1.3	Basis of the method	Extraction of the sample with 0.05 M EDTA followed by determination of the extracted metals by flame atomic absorption spectrophotometry.
A1.4	Range of application	Cadmium up to 5.0 mg/kg Zinc up to 10.0 mg/kg Copper and manganese up to 25.0 mg/kg Lead and nickel up to 50.0 mg/kg
A1.5	Calibration curve	Normally linear in the ranges stated in A1.4 except for zinc
A1.6	Standard deviation	
A1.6.1	Within batch standard deviation (a)	

Soil No		1	2	3	4	5	6	7	8
Cadmium (mg/kg)		0.08	0.14	0.08	0.14	0.12	0.07	0.17	0.09
SD (mg/kg)		0.01	0.01	0.01	0.01	0.04	0.00	0.00	0.00
DOF		1	1	1	1	1	1	2	2
Copper (mg/kg)		1.61	1.64	3.05	2.97	2.74	1.04	7.86	3.97
SD (mg/kg)		0.07	0.12	0.14	0.16	0.20	0.10	0.66	0.29
DOF		6	6	6	6	6	6	10	10
Lead (mg/kg)		2.60	5.61	4.79	5.02	4.16	2.96	15.80	11.10
SD (mg/kg)		0.20	0.46	0.57	0.42	0.37	0.30	1.33	0.94
DOF		4	4	4	4	4	4	5	5
Manganese (mg/kg)		46.5	34.5	52.6	30.2	19.0	21.9	77.9	79.7
SD (mg/kg)		3.7	4.4	7.5	3.1	1.2	1.3	6.8	4.9
DOF		6	6	6	6	6	6	10	10
Nickel (mg/kg)								2.13	2.16
SD (mg/kg)								0.09	0.05
DOF								3	3
Zinc (mg/kg)		0.88	1.82	1.93	0.97	0.91	0.84	11.9	2.42
SD		0.09	0.16	0.19	0.10	0.07	0.11	1.0	0.21
DOF		6	6	6	6	6	6	10	10

A1.6.2 Total standard deviation (b)

Element	Concentration (mg/kg)	Total standard deviation (mg/kg)	Degrees of freedom	No. of laboratories
Copper	5.65	0.04 – 2.92	5 – 9	48
Nickel	2.10	0.04 – 0.49	5 – 9	46
Zinc	7.29	0.10 – 2.83	5 – 9	46

The mean relative total standard deviations for copper, nickel and zinc are 9.2, 9.6 and 11.4% respectively.

A1.7	Limit of detection	Cadmium	0.10 mg/kg
		Copper	0.15 mg/kg
		Lead	0.25 mg/kg
		Manganese	0.25 mg/kg
		Nickel	0.50 mg/kg
		Zinc	0.05 mg/kg
A1.8	Sensitivity (for 1% absorption)	Cadmium	0.10 mg/kg
		Copper	0.30 mg/kg
		Lead	0.60 mg/kg
		Manganese	0.50 mg/kg
		Nickel	0.50 mg/kg
		Zinc	0.25 mg/kg
A1.9	Bias	Not known but see Sections A6.4 and A8.1. In the interlaboratory study (b) the mean (absolute) deviations of individual laboratory's results from the relevant overall means were 7.1% for copper, 10.9% for nickel and 8.4% for zinc.	
A1.10	Interferences	See Section A3	
A1.11	Time required for analysis	For 18 simultaneous extractions the analytical time is 4 hours and the operator time is 3 hours 15 minutes. For 3 elements to be determined using flame atomic absorption the analytical time is approximately 3 hours for the 18 extracts.	

(a) This data was obtained by the Macaulay Institute for Soil Research⁽²⁾(³). For manganese the filtrates were diluted (see Section A10).

(b) This data was obtained during a collaborative analysis of sewage sludge and soils organised by the Water Research Centre⁽⁴⁾. The same soil sample was analyzed ten times by 48 laboratories for copper and 46 laboratories for nickel and zinc. The soil sample was ground to pass through a 0.5 mm sieve and then mixed. The method described in this booklet was used but not all laboratories extracted at a temperature of $20 \pm 1^\circ\text{C}$.

A2. Principle

The metals are extracted from the sample with 0.05M ammonium ethylenediamine tetracetate solution (EDTA) at pH 7.0. The concentration of the metals in the extract is determined by flame atomic absorption spectrophotometry.

A3. Interferences

Spectral interference can occur when undissociated molecular species in the atomiser absorb light at the same wavelength used for atomic absorbance. These effects are particularly severe in the wavelength region below about 250nm. Additional apparent absorption arising from other effects, such as the scattering of light from the line source by high concentrations of inorganic salts, may also occur. Automatic background correction systems are available in most recent instruments to control these "non-atomic" effects.

A4. Hazards

Ammonia gas and ammonia solution are hazardous (see Section A5.2). The gas or vapour is toxic by inhalation and severely irritates the eyes and respiratory system. If the solution enters the eyes, irrigate thoroughly with water and obtain medical attention as soon as possible. The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away.

A5. Reagents

All reagents and standard solutions should be kept in polyethylene bottles unless otherwise stated. Analytical reagent grade chemicals are suitable unless otherwise specified. It is preferable that all standard solutions be prepared from freshly cleaned metal. Standard solutions prepared by commercial organisations are also available and satisfactory.

A5.1 Water

The water used to prepare the reagents and standard solutions should have metal contents that are negligible relative to the lowest concentration to be determined in the samples. 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 Ammonia solution (d_{20} 0.88)

Analytical grade ammonia solution (d_{20} 0.88, about 35% NH_3) may be used provided that it is acceptably low in the metals to be determined. Otherwise the ammonia solution should be prepared as follows:

Ammonia solution (d_{20} 0.92)

Ammonia gas from a commercial liquid ammonia cylinder, controlled by a mild steel needle-valve, is gently bubbled into 1500 ml of glass distilled water contained in a borosilicate vessel within a fume cupboard. The volume increases during the dissolution period and on cooling should be slightly greater than 2000 ml. When bubbles of ammonia gas reach the surface of the liquid the solution is saturated. This is normally after a period of 10 hours. An appropriate safety trap, capable of containing the total volume of solution, placed between the needle-valve and the receiver prevents suck-back of the solution into the cylinder. Store in a polyethylene container in a cool place.

A5.3 0.05M EDTA as an ammonium salt solution

Add 146.12 ± 0.05 g of EDTA free acid to 800 ± 20 ml of water and partially dissolve by stirring in 130 ± 5 ml of ammonia solution (d_{20} 0.92) or 93 ± 2 ml (d_{20} 0.88). Continue the addition of further ammonia solution drop by drop until all the EDTA has just dissolved. Filter through a suitable filter paper of porosity $1.4 - 2.9 \mu\text{m}$ (capable of retaining particles of $8.0 \mu\text{m}$ size) into a 10-litre polyethylene container. Dilute with water to 9.0 ± 0.5 litres. Adjust the pH value to 7.00 ± 0.05 by the addition of a few drops of either ammonia solution or hydrochloric acid (d_{20} 1.18) as appropriate, dilute with water to 10.0 ± 0.1 litres and mix well. Store in a polyethylene container. Prepared by this procedure the extracting solution is virtually free from copper contamination.

Alternatively dissolve 181.17 ± 0.05 g of EDTA diammonium salt (spectroscopic grade) in water, dilute with water to 9.0 ± 0.5 litres, adjust the pH to 7.00 ± 0.05 by addition of ammonia solution and dilute with water to 10.0 ± 0.1 litres. Mix well and store in a polyethylene container.

A5.4 50% V/V Hydrochloric acid

Dilute 500 ± 5 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

A5.5 50% V/V Nitric acid

Dilute 500 ± 5 ml of nitric acid (d_{20} 1.42) with water to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

A5.6 Standard cadmium solutions

A5.6.1 Solution A 1 ml contains 20 mg Cd.

Weigh 1.000 ± 0.005 g of cadmium wire (greater than 99.9% purity) and dissolve with gentle heating in a mixture of 7.0 ± 0.5 ml of nitric acid (d_{20} 1.42) and approximately 20 ml of water. Quantitatively transfer the solution to a 1-litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

A5.6.2 Solution B 1 ml contains 20 µg Cd.

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

A5.7 Standard copper solutions

A5.7.1 Solution A 1 ml contains 1 mg Cu.

Weigh 1.000 ± 0.005 g copper metal (greater than 99.9% purity) and dissolve with gentle heating in a minimum volume of 50% V/V nitric acid. Quantitatively transfer the solution to a 1-litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

A5.7.2 Solution B 1 ml contains 20 µg Cu.

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

A5.8 Standard lead solutions

A5.8.1 Solution A 1 ml contains 1 mg Pb.

Weigh 1.000 ± 0.005 g lead wire (greater than 99.9% purity) and dissolve with gentle heating in a mixture of 7.0 ± 0.5 ml of nitric acid (d_{20} 1.42) and approximately 20 ml of water. Quantitatively transfer the solution to a 1-litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

A5.8.2 Solution B 1 ml contains 20 µg Pb.

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

A5.9 Standard manganese solutions.

A5.9.1 Solution A 1 ml contains 1 mg Mn.

Weigh 1.000 ± 0.005 g of manganese metal (greater than 99.9% purity) and dissolve with gentle heating in a minimum volume of 50% V/V nitric acid. Quantitatively transfer the solution to a 1-litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

A5.9.2 Solution B 1 ml contains 20 µg Mn.

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

A5.10 Standard nickel solutions.

A5.10.1 Solution A 1 ml contains 1 mg Ni.

Weigh 1.000 ± 0.005 g of nickel metal (greater than 99.9% purity) and dissolve with gentle heating in a minimum volume of 50% V/V nitric acid. Quantitatively transfer the solution to a 1-litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

A5.10.2 Solution B 1 ml contains 20 µg Ni.

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

A5.11 Standard zinc solutions

A5.11.1 Solution A 1 ml contains 1 mg Zn.

Weigh 1.000 ± 0.005 g of zinc metal (greater than 99.9% purity) and dissolve with gentle heating in 40 ± 1 ml of 50% V/V hydrochloric acid. Quantitatively transfer the solution to a 1-litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

A5.11.2 Solution B 1 ml contains 20 µg Zn.

Dilute 20.0 ± 0.1 ml of solution A with 0.05 M EDTA solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

A5.12 Working Standard Solutions

Prepare a range of working standard solutions for each element covering the anticipated concentrations of each element in the extracts by diluting appropriate amounts of the appropriate standard solutions B with 0.05 M EDTA solution. These working standard solutions should be prepared freshly when required (see Section A8.5). A suitable composite working standard solution may be used.

A6. Apparatus

A6.1 Laboratory ware

Before carrying out each batch of determinations all laboratory glass and polyethylene ware used in the procedure should be cleaned with 50% V/V hydrochloric acid, rinsed with water, cleaned with 0.05 M EDTA solution and finally rinsed with water. Rubber stoppers and plastic materials containing zinc or cadmium must not be used in this determination.

A6.2 An atomic absorption spectrophotometer equipped with an air/acetylene flame and hollow cathode lamps for cadmium, copper, lead, manganese, nickel and zinc and with facilities for manual or automatic background correction.

A6.3 Extraction bottles of 250 ml capacity made of borosilicate glass with glass stoppers. Polypropylene or polyethylene bottles with caps without inserts are also suitable.

A6.4 A mechanical shaking apparatus. A suitable apparatus is the Griffin silent shaking machine obtainable from Griffin and George Ltd (Catalogue No. S 36-650). This apparatus is a reciprocating shaker and should be set to the medium throw position. Other types of shaking machine are available (such as end-over-end, gyratory, wrist action etc) but the reciprocating shaker is preferred. The results obtained are dependent on the type of shaker used and the temperature of extraction.

A7. Sample collection, preservation and initial preparation

A6.5 Filter stands and funnels. Filter stands should preferably be made from polypropylene and filter funnels from borosilicate glass or polypropylene to minimise metallic contamination.

The methods of sample collection, preservation and initial preparation are described in another publication in this series⁽¹⁾.

A8. Analytical procedure

READ SECTION A4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
Extraction Stage		
A8.1	Prepare a dry sample (see Section A7) and transfer 15.0 ± 0.1 g (note a) into an extraction bottle. Add 75 ± 1 ml 0.05 M EDTA extracting solution and immediately shake for $1 \text{ hour} \pm 2$ minutes at a temperature of $20 \pm 1^\circ\text{C}$ (note b). Immediately filter through a pre-rinsed (with 0.05M EDTA followed by water and left to drain) 18.5 cm cellulose hardened ashless filter paper of porosity 0.4 to $1.1 \mu\text{m}$ capable of retaining particle sizes of $2.7 \mu\text{m}$. Collect and retain sufficient filtrate for the atomic absorption stage.	(a) The subsample required for analysis is obtained by placing the whole sample on a polyethylene sheet and coning and quartering until approximately the required weight is reached. (b) It is important, in order to obtain consistent results, that the time of shaking and temperature are strictly adhered to.
Determination of the density of the dry sample		
A8.2	Determine the density of the dry sample by weighing several 20 ml portions of the dry sample (measured using a 20 ml scoop-filled and struck off level without tapping). Divide the weights obtained in grams by 20 (note c). Determine the average density.	(c) The density is required if the concentration of metals needs to be expressed on a m/V basis.

Blank determination

- A8.3 A blank must be carried out with each batch (eg up to 12 samples) of determinations using the same batch of reagents as for samples. Add 75 ± 1 ml of 0.05 M EDTA extracting solution to an extraction bottle and carry out the shaking and filtration part of step A8.1.

Atomic absorption stage

- A8.4 Set up the atomic absorption spectrophotometer as detailed in the manufacturers handbook. Perform all the determinations (ie samples, blanks and standards) for one element; then perform all the determinations for the rest of the elements sequentially.

Calibration standards

- A8.5 Duplicate calibration standards for each element (except zinc) must be run with each batch (eg up to 12 samples) of determinations. For zinc, it is necessary to prepare a calibration curve with each batch of determinations.

For each element the following calibration standards are required and should be freshly prepared by diluting the stated volume of the appropriate standard solution B to 100 ml with 0.05 M EDTA.

<i>Element</i>	<i>Concentrations (mg/l)</i>	<i>Solutions B (ml)</i>	
Cadmium	1.0	5.00 ± 0.05	(d) These first five standards can be mixed.
Copper	5.0	25.00 ± 0.10	
Manganese	5.0	25.00 ± 0.10	
Lead	10.0	50.00 ± 0.10	
Nickel	10.0	50.00 ± 0.10	
(note d)			

<i>Element</i>	<i>Concentrations (mg/l)</i>	<i>Solution B (ml)</i>	
Zinc	0.0	0.00	
"	0.4	2.00 ± 0.02	
"	0.8	4.00 ± 0.03	
"	1.2	6.00 ± 0.05	
"	2.0	10.00 ± 0.10	

- A8.6 The wavelengths required are:—

Cadmium	228.8 nm
Copper	324.7 nm
Lead	217.0 nm
Manganese	279.5 nm
Nickel	232.0 nm
Zinc	213.9 nm

Method of measurement

- A8.7 For each element in sequence. Aspirate water and adjust the zero. Aspirate one of the calibration standards (2.0 mg/l for zinc) and adjust the instrument to give a suitable response. Aspirate water and adjust the zero if necessary.

- A8.8 Aspirate both the calibration standards (all the calibration standards for zinc) with an aspiration of water after each and measure the instrument responses C_1 and C_2 (for zinc measure the instrument responses, prepare a calibration curve and see Section A8.11 for the calculation of the result). Aspirate the blank and measure the instrument response B_1 and then aspirate water.
- A8.9 Aspirate the samples (note e) (see Section A10) with an aspiration of water after each and measure the instrument response of the sample. The instrument response for each sample must be corrected for background absorption. If the instrument is not equipped to perform this correction automatically then a separate measurement for background must be made using a suitable continuum source. Let the response of the sample corrected for background be S .
- (e) Some extracts may require dilution with 0.05M EDTA to bring their metal concentrations within the working range. The dilution factor must be allowed for when calculating the result.
- A8.10 To check for any instrument drift aspirate both the calibration standards (2.0 mg/l for zinc) and the blank with an aspiration of water after each and measure the instrument responses C_3 , C_4 and B_2 respectively.

Calculation of results

- A8.11 Calculate the concentration of each metal, M , in the sample for each element from

$$M = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times F \text{ mg/kg}$$

$$\text{where } \bar{B} = \frac{B_1 + B_2}{2}$$

$$\bar{C} = \frac{C_1 + C_2 + C_3 + C_4}{4}$$

$$F = \begin{array}{l} 5.0 \text{ for cadmium} \\ 25.0 \text{ for copper and manganese} \\ 50.0 \text{ for lead and nickel} \end{array}$$

These calculations assume a linear calibration curve (see Section A9).

For zinc read the concentration of zinc in the extract, Z mg/l, from the calibration graph then

$$M = Z \times 5 \text{ mg/kg}$$

- A8.12 If the concentration of each metal, is required to be expressed in % m/V then multiply the result from step A8.11 by the density of the dry sample (step A8.2).

A9. Checking the linearity of the calibration curve

A9.1 The procedure given in this Section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.

A9.2 For each element freshly prepare a series of calibration standards by diluting the stated volumes of the appropriate standard *Solution B* to 100 ml with 0.05M EDTA. Carry out the procedure given in steps A8.4 and A8.6 to A8.8 inclusive and plot the instrument response against the concentration of the element.

Element	Concentration (mg/l)	Solution B (ml)
Cadmium	0.00, 0.05, 0.10, 0.20, 0.50 and 1.00	0.00, 0.25, 0.50, 1.00, 2.50 and 5.00
Copper and Manganese } Lead and Nickel }	0.00, 0.05, 0.10, 0.50, 1.00, 2.00 and 5.00 0.00, 0.20, 0.50, 1.00, 2.00, 5.00 and 10.00	0.00, 0.25, 0.50, 2.50, 5.00, 10.00 and 25.00 0.00, 1.00, 2.50, 5.00, 10.00, 25.00 and 50.00

A9.3 For all these elements (except zinc) the calibration curve is normally linear in the range stated; however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve departs from linearity, as it does for zinc, then a calibration curve must be prepared with each batch of determinations and the concentration of metal in the extract read from the calibration curve.

A10. Change in concentration range of the method

The range of application of the method is as follows:—

Cadmium	up to 5.0 mg/kg
Zinc	up to 10.0 mg/kg
Copper and Manganese	up to 25.0 mg/kg
Lead and Nickel	up to 50.0 mg/kg

If the concentrations of the metals are likely to exceed the quoted ranges then V_1 ml of the extraction solution filtrate (from step A8.1) should be diluted with 0.05M EDTA to an appropriate volume V_2 ml. This dilution factor must be taken into account in the calculation of the result by multiplying by $\frac{V_2}{V_1}$.

A11. References

- (1) Methods for the Examination of Waters and Associated Materials, The Sampling and Initial Preparation of Sewage and Waterworks' Sludges, Soils, Sediments and Plant Material Prior to Analysis, HMSO, 1977. *
- (2) Ure AM and Berrow ML, *Anal. Chim. Acta*, 52, 1970, 247–257.
- (3) Department of the Environment, File WS/646/151, Paper SCA/46/Ext 2.
- (4) Water Research Centre, Final Contract Report to the Department of the Environment 41-M, 1981 (paper SCA/8.0/81).

* See also Additions and Corrections 1983, to be published in this series.

B. Nickel and Zinc Extractable by 0.5M Acetic Acid in Soils, Sewage Sludge Treated Soils and Related Materials

B1 Performance characteristics of the method

(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Results 1980, also published in this series.)

B1.1	Substances determined	Extractable nickel and zinc			
B1.2	Type of sample	Soils, sewage sludge treated soils and related materials			
B1.3	Basis of the method	Extraction of the sample with 0.5M acetic acid followed by determination of the extracted metals by atomic absorption spectrophotometry. The method is not suitable for calcereous soils.			
B1.4	Range of application	Nickel	up to 80 mg/kg		
		Zinc	up to 80 mg/kg		
B1.5	Calibration curve	Normally linear for nickel in the range stated in B1.4. Zinc may be non-linear.			
B1.6	Total standard deviation (a)	Element	Concentration (mg/kg)	Total standard deviation (mg/kg)	Degrees of freedom
		Nickel	2.30	0.03–1.14	5–9
		Zinc	8.92	0.08–2.97	5–9
		The mean relative total standard deviations are 25.5% for nickel and 12.3% for zinc.			
B1.7	Limit of detection	Nickel	1.25 mg/kg		
		Zinc	0.30 mg/kg		
B1.8	Sensitivity (for 1% absorption)	Nickel	4.00 mg/kg		
		Zinc	0.80 mg/kg		
B1.9	Bias	Not known but see Sections A6.4 and B8.1. In the interlaboratory study (a), the mean (absolute) deviations of individual laboratory's results from the relevant overall means were 20.1% for nickel and 15.6% for zinc.			
B1.10	Interferences	See Section B3.			
B1.11	Time required for analysis	For 18 simultaneous extractions the analytical time is 4 hours and the operator time is 3 hours excluding the overnight shaking period.			
		For 2 elements to be determined using flame atomic absorption the analytical time is approximately 2 hours for the 18 extracts.			

(a) This data was obtained during a collaborative analysis of sewage sludge and soils organised by the Water Research Centre^(?). The same soil was analysed 10 times by 42 laboratories for nickel and 47 laboratories for zinc. The soil sample was ground to pass through a 0.5 mm sieve and then mixed. The method described in this booklet was used but not all laboratories extracted at $20 \pm 2^\circ\text{C}$.

- B2. Principle** The metals are extracted from the sample with 0.5M acetic acid. The concentration of the metals in the extract is determined by atomic absorption spectrophotometry.
- B3. Interferences** As for Method A, Section A3.
- B4. Hazards** The fumes from the atomic absorption spectrophotometer are toxic and must be ducted away.
- B5. Reagents** All reagents and standard solutions must be stored in polyethylene bottles unless otherwise stated. Analytical reagents grade chemicals as suitable unless otherwise specified.
- B5.1 Water**
As for Method A, Section A5.1.
- B5.2 0.5M Acetic Acid**
Dilute 30 ± 1 ml of glacial acetic acid (d_{20} 1.049) with water to 1 litre in a measuring cylinder.
- B5.3 50% V/V Hydrochloric acid**
Dilute 500 ± 5 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder.
- B5.4 50% V/V Nitric acid**
Dilute 500 ± 5 ml of nitric acid (d_{20} 1.42) with water to 1 litre in a measuring cylinder.
- B5.5 Standard nickel solutions**
- B5.5.1 Solution A 1 ml contains 1 mg Ni*
As for Method A, Section A5.10.1
- B5.5.2 Solution B 1 ml contains 20 µg Ni.*
Dilute 20.0 ± 0.1 ml of solution A with 0.5M acetic acid solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.
- B5.6 Standard zinc solutions**
- B5.6.1 Solution A 1 ml contains 1 mg Zn*
As for Method A, Section A5.11.1
- B5.6.2 Solution B 1 ml contains 20 µg Zn.*
Dilute 20.0 ± 0.1 ml of Solution A with 0.5M acetic acid solution to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.
- B5.7 Working Standard Solutions**
Prepare a range of working standard solutions for each element covering the anticipated concentrations of each element in the extracts by diluting appropriate amounts of the appropriate standard solutions B with 0.5M acetic acid. These working standard solutions should be freshly prepared when required (see Section B8.5)
- B6. Apparatus**
- B6.1 Laboratory ware**
Before carrying out each batch of determinations all laboratory glass and polyethylene ware used in the procedure should be cleaned with 50% V/V hydrochloric acid, rinsed with water, cleaned with 0.5M acetic acid solution and finally rinsed with water. Rubber stoppers or plastic materials containing zinc must not be used in this determination.
- B6.2 Atomic absorption spectrophotometer** equipped with an air/acetylene flame and hollow cathode lamps for nickel and zinc and with facilities for manual or automatic background correction.

B6.3 As for Method A, Section A6.3.

B6.4 As for Method A, Section A6.4

B6.5 As for Method A, Section A6.5

B7. Sample collection, preservation and initial preparation

The methods of sample collection, preservation and initial preparation are described in another publication in this series⁽¹⁾.

B8. Analytical procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
Extraction Stage		
B8.1	Prepare a dry sample (see Section B7) and transfer 5.00 ± 0.05 g (note a) into an extraction bottle. Add 200 ± 2 ml of 0.5M acetic acid extracting solution. Shake by hand for a few minutes, frequently releasing any pressure arising from the liberation of carbon dioxide and then shake on a mechanical shaker for 16 hours \pm 30 minutes, preferably at $20 \pm 2^\circ\text{C}$. (note b). Immediately filter through a pre-rinsed (with 0.5M acetic acid followed by water and allowed to drain) 18.5 cm cellulose hardened ashless filter paper of porosity 0.4 to $1.1\mu\text{m}$ capable of retaining particle sizes of $2.7\mu\text{m}$. Collect and retain sufficient filtrate for the atomic absorption stage.	(a) The subsample required for analysis is obtained by placing the whole sample on a polyethylene sheet and coning and quartering until approximately the required weight is reached. (b) It is important, in order to obtain consistent results, that the time of shaking and temperature are strictly adhered to.
Determination of the density of the dry sample		
B8.2	Determine the density of the dry sample by weighing several 20 ml (using a 20 ml scoop filled and struck off level without tapping) of the dry sample. Divide the weights obtained in grams by 20 (note c). Determine the average density.	(c) The density is required if the concentration of metals needs to be expressed on a m/V basis.
Blank determination		
B8.3	A blank determination must be carried out on each batch (eg up to 12 samples) of determinations using the same batch of reagents as for samples. Add 200 ± 2 ml of 0.5M acetic acid extracting solution to an extraction bottle and carry out the shaking and filtration part of step B8.1.	
Atomic absorption stage		
B8.4	Set up the atomic absorption spectrophotometer as detailed in the manufacturers handbook. Perform all the determinations (ie samples, blanks and calibration standards) for one element; then perform all the determinations for the other element sequentially.	
Calibration standards		
B8.5	A duplicate calibration standard must be run with each batch (eg up to 12 samples) of determinations for nickel. For zinc it is necessary to prepare a calibration curve with each batch of determinations. For each element the following calibration standards are required and should be freshly prepared by diluting the stated volume of the appropriate standard solution B to 100 ml with 0.5M acetic acid.	

Element	Concentration (mg/l)	Solution B (ml)
Nickel	2.0	10.00 ± 0.10
Zinc	0.0	0.00
"	0.4	2.00 ± 0.02
"	0.8	4.00 ± 0.03
"	1.2	6.00 ± 0.05
"	1.6	8.00 ± 0.05
"	2.0	10.00 ± 0.10

B8.6 The wavelengths required are:

Nickel	232.0 nm
Zinc	213.9 nm

Method of measurement

B8.7 For each element in sequence. Aspirate water and adjust the zero. Aspirate one of the calibration standards (2.0 mg/l for zinc) and adjust the instrument to give a suitable response. Aspirate water and adjust the zero if necessary.

B8.8 Aspirate both the calibration standards (all the calibration standards for zinc) with an aspiration of water after each and measure the instrument responses C_1 and C_2 (for zinc measure the instrument responses, prepare a calibration curve and see Section B8.11 for the calculation of the result). Aspirate the blank and measure the instrument response B_1 and then aspirate water.

B8.9 Aspirate the samples (note d) (see Section B10) with an aspiration of water after each and measure the instrument response of the sample.

(d) Some extracts may require dilution with 0.5M acetic acid to bring their metal concentrations within the working range. The dilution factor must be allowed for when calculating the result.

The instrument response for each sample must be corrected for background absorption. If the instrument is not equipped to perform this correction automatically then a separate measurement for background must be made using a suitable continuum source. Let the response of the sample corrected for background be S.

B8.10 To check for any instrument drift aspirate both the calibration standards (2.0 mg/l for zinc) and the blank with an aspiration of water after each and measure the instrument responses C_3 , C_4 and B_2 respectively.

Calculation of results

B8.11 Calculate the concentration of nickel, M, in the sample from

$$M = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 80 \text{ mg/kg}$$

$$\text{where } B = \frac{B_1 + B_2}{2}$$

$$\bar{C} = \frac{\bar{C}_1 + C_2 + C_3 + C_4}{4}$$

This calculation assumes a linear calibration curve (see Section B9)

For zinc read the concentration of zinc in the extract, Z mg/l, from the calibration graph then

$$M = Z \times 40 \text{ mg/kg}$$

- B8.12 If the concentration of each metal is required to be expressed in % m/V then multiply the result from step B8.11 by the density of the dry sample (step B8.2).

B9. Checking the linearity of the calibration curve

B9.1 Before application of this method to any samples the procedure given in the Section must be carried out on at least two independent occasions and regularly thereafter.

B9.2 For each element freshly prepare a series of calibration standards by diluting the stated volumes of the appropriate standard *Solution B* to 100 ml with 0.5M acetic acid. Carry out the procedure given in steps B8.4 and B8.6 to B8.8 inclusive and plot the instrument response against the concentration of the element.

Element	Concentrations (mg/l)	Solution B (ml)
Nickel	0.0, 0.4, 0.8, 1.2, 1.6 and 2.0	0.0, 2.0, 4.0, 6.0, 8.0 and 10.0
Zinc	0.0, 0.4, 0.8, 1.2, 1.6 and 2.0	0.0, 2.0, 4.0, 6.0, 8.0 and 10.0

B9.3 For nickel the calibration curve is normally linear in the range stated; however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve departs from linearity, as it does for zinc, then a calibration curve must be prepared with each batch of determinations and the concentration of metal in the extract read from the calibration curve.

B10. Change in concentration range of the method

The range of application of the method is as follows:—

Nickel	up to 80.0 mg/kg
Zinc	up to 80.0 mg/kg

If the concentrations of the metals are likely to exceed the quoted ranges then V_1 ml of the extraction solution filtrate (from step B8.1) should be diluted with 0.5M acetic acid to an appropriate volume V_2 ml. This dilution factor must be taken into account in the calculation of the result by multiplying by $\frac{V_2}{V_1}$.

B11. References

- (1) Methods for the Examination of Waters and Associated Materials, The Sampling and Initial Preparation of Sewage and Waterworks' Sludges, Soils, Sediments and Plant Material prior to Analysis, HMSO, 1977.*
- (2) Water Research Centre, Final Contract Report to the Department of the Environment 41-M, 1981 (paper SCA/8.0/81)

* See also Additions and Corrections 1983, to be published in this series.

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