Lead and Cadmium in Fresh Waters by Atomic Absorption Spectrophotometry (Second Edition)
A General Introduction to Electrothermal Atomization Atomic Absorption Spectrophotometry 1986

Methods for the Examination of Waters and Associated Materials

Her Majesty's Stationery Office

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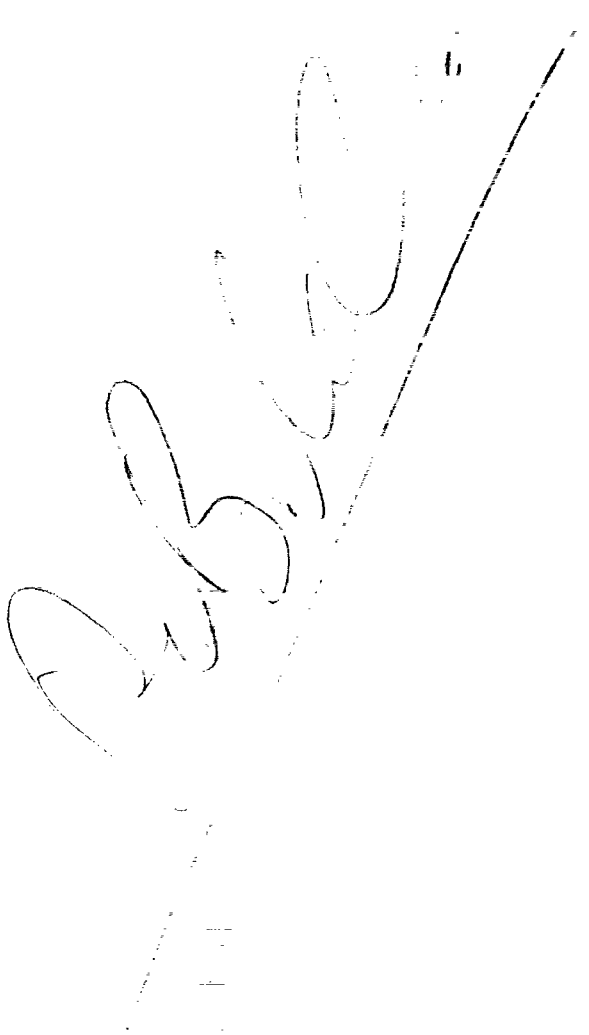
This booklet contains in Part C the methods issued originally in 1976. These have been combined into one text with a little additional data.

The booklet begins with a general review of Electrothermal Atomization Atomic Absorption Spectrophotometry (EAAS). This is followed by an EAAS method for lead and cadmium (Part B). The final method (Part D) is an alternative solvent extraction procedure for lead, which although it has not been tested for cadmium, might be used for such analysis after suitable testing. This latter procedure avoids the use of MIBK.

Contents



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 These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print.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 users 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 nonmetallic 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

1 July 1986

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 waste, 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 Practices 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 required 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.

A General Introduction to Electrothermal Atomization Atomic Absorption Spectrophotometry

This review is a general introduction to EAAS, in which the advantages and limitations of the types of electrothermal atomization and the main instrumental variables are discussed. This is followed in Part B by general procedure for lead and cadmium including some performance characteristics obtained under typical operating conditions. This procedure must only be used as a guide because each analyst must carry out detailed optimization of instrumental conditions for his particular instrument. Also lanthanum is added to samples to reduce the interference effects to which the technique is subject and although it is effective it does not eliminate such effects completely and its effectiveness may vary with the type of instrument used.

A1 Introduction

A1.1 The limits of detection required for raw and potable water analysis can be taken as approximately one tenth of the mandatory limits set by the European Community in its Directives concerning the quality of surface water intended for the abstraction of drinking water(1) (and its daughter directive concerning the methods of measurement and frequency of sampling and analysis(2) and the quality of water intended for human consumption(3). Some of these values are given in Table A1, as well as some typical flame and electrothermal atomization and flame atomic absorption spectrophotometry limits of detection.

It can be seen from this Table that generally direct flame AAS is not suitable for this type of analysis. Also the UK will be applying the concept of Environmental Quality Standards (EQS) to comply with directives derived from the EC Directive on pollution discharged into the aquatic environment. It is likely that in many cases for the common metals the EQS levels will be too low for direct flame AAS.

A1.2 The sensitivity of conventional flame techniques is limited by the fact that only 3–10% of the nebulized sample reaches the flame whereupon it immediately undergoes considerable dilution by the flame gases. For example, a typical nebulizer may have a sample uptake rate of 4ml/min of which 0.2 ml/min will reach the flame. A typical air-acetylene flame will consume about 10 litres/min of flame gases. Thus the sample is effectively diluted about 50,000 times.

A1.3 If an aliquot of the analyte solution were evaporated to dryness and the residue were to be rapidly vaporized and atomized, a large increase in sensitivity would be expected. This can be achieved by adding a small volume (normally 2–50µl) of the sample to a graphite tube or rod maintained in an inert atmosphere. A small controlled current is passed through the device to evaporate the solvent (evaporation stage) followed by a larger current to dry ash the sample without loss of analyte (dry ashing stage) and finally a much larger current heats the device to a suitable temperature to atomize and vaporise the analyte (atomization stage). During this stage the transient atomic absorption signal is monitored. This inherently simple technique generally referred to as electrothermal atomization results in a significant improvement in the limits of detection for a large number of elements as shown in Table A1.

Table A1 Mandatory Limits in European Community Directives and UK Water Quality Standards arising from European Community Directives compared with Typical Limits of Detection for Flame and Electrothermal AAS Techniques.

Element	Mandatory Limit (μg/litre) Drinking Water		Lowest Limit value (μg/litre) quoted in reference given in note 3 for the protection of fish or other aquatic life in fresh water		Typical Limit of Detection (μg/litre) Flame AAS	Electrothermal AAS
		(1)	(2)	(3)		
As	50	(2–10)	50	50	1000–2500	0.5–2
Al	–	–	200	–	100–250	0.2–1
Ba	100	(20)	–	–		0.4–1
Cd	5	(0.2–1)	5	5	2–5	0.05–0.2
Cr	50	(10)	50	5	20–50	0.01–0.3
Cu	50	(5–20)	100	1	5–15	0.05–0.15**
Fe	300*	(20)	200	–	15–30	0.1–0.3**
Mo	–	–	–	–		0.6–2.0
Ni			50	8		0.3–1.0
Pb	50	(10)	50	4	25–50	0.3–1.0
V	–	–	–	–		1.5–5.0
Zn	3000	(10–20)	100	10	2–5	0.2**

* Dissolved iron.
** Usually limited by contamination.

Note: Limits of detection assume the use of automatic background correction and a typical sample batch injection volume of 10–20 μg/l.

1. EC Directive concerning the quality required of surface water intended for abstraction of drinking water(1) (for category A1 waters) with the figures in brackets being the limits of detection (defined as the minimum value which it is possible to detect) from the daughter EC Directive concerning methods of measurement and frequencies of sampling and analysis(2).

2. EC Directive relating to the quality of water intended for human consumption(3).

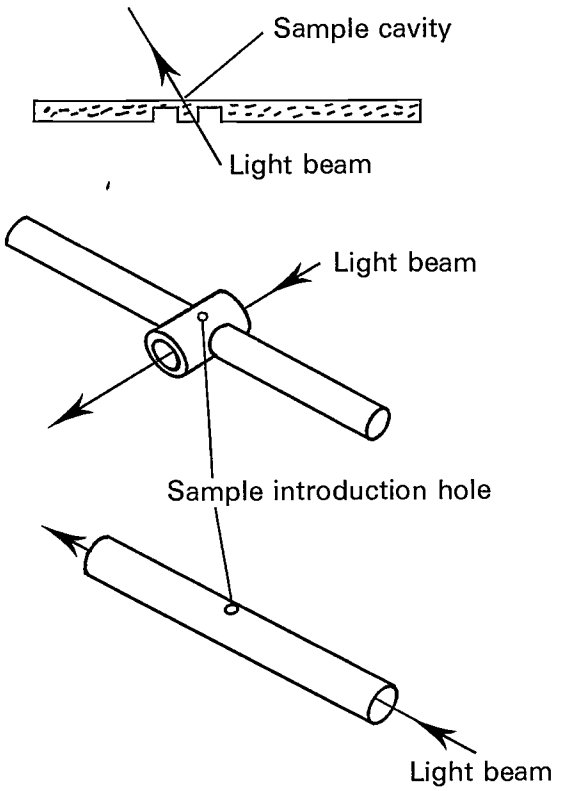
3. From Gardiner F. and Mance G., UK Water Quality Standards Arising from EC Directive. WRc Technical Report TR 204, July 1984.

A2 Types of Electrothermal Atomization

A2.1 The three most common forms of commercially available graphite based electrothermal atomizers are depicted in Figure A1. Almost all the latest atomizers are of the graphite tube type (Figure A1c). Other materials such as tungsten, tantalum and molybdenum have been used in the past, but these materials are more prone to attack by certain acids and tend to become brittle with age. It is now generally agreed that these materials are inferior to graphite.

A2.2 Figure A2 depicts a graphite tube electrothermal atomizer. The maximum operating temperature is approximately 3000°C. The graphite is shielded with argon or nitrogen to prevent oxidation by air. Most manufacturers offer graphite tubes coated with pyrolytic graphite. These tubes have several advantages, namely improved sensitivity and reduced memory effects for refractory carbide forming elements such as Molybdenum, silicon, titanium and vanadium; greater resistance to oxidizing mineral acids and longer lifetime at high operating temperatures. It is possible to coat standard graphite tubes with pryolytic graphite in situ by heating the tube to approximately 2000°C in the presence of a small quantity of methane(4,5). Non-pyrolytic tubes can be satisfactorily used for non-carbide forming elements such as cadmium, copper and lead. At least one manufacturer offers tubes fabricated solely from pyrolytic graphite. The useful operating lifetime of these tubes is claimed to be significantly greater than that of uncoated or pyrolytically coated tubes.

Figure A1 Diagrammatic representation of various types of graphite based flameless electrothermal atomization devices



(a)

Graphite rod atomizer
(typical sample volumes 2 - 10 μl)

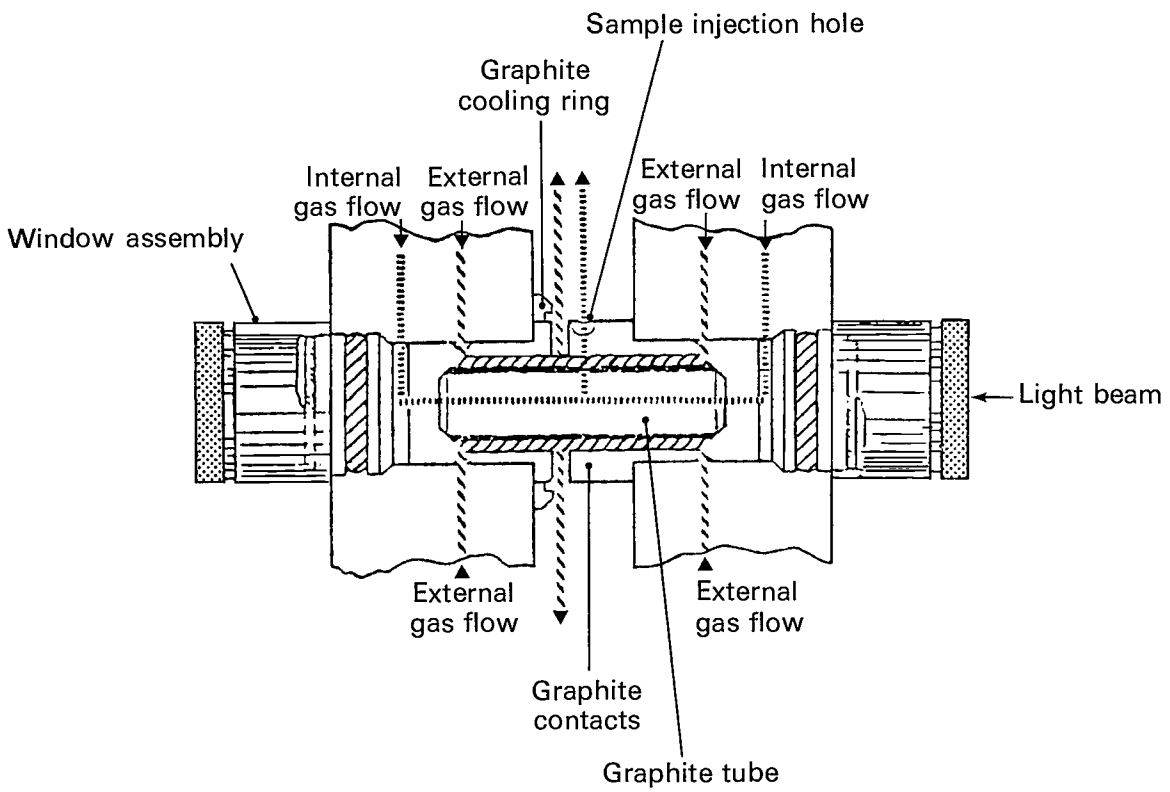
(b)

Minature graphite tube atomizer (mini-Massmann)
(typical sample volumes 5 - 20 μl)

(c)

Standard graphite tube atomizer (Massmann)
(typical sample volumes 10 - 100 μl)

Figure A2 Graphite tube atmomizer



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A3. Operating Considerations

A3.1 Shield Gas

Nitrogen is generally used but if nitride forming elements such as barium, molybdenum, titanium and vanadium are to be determined, argon is the preferred gas. In order to minimize condensation of analyte and matrix volatilization products on the cooler ends of the graphite tube, the inert shield gas is usually introduced at the ends of the graphite tube and exits from the sample introduction hole (Figure A2). The optimum gas flow(s) are normally specified by the manufacturer and in some units can be automatically reduced or stopped during the atomization stage. This results in increased sensitivity and can reduce certain interelement effects.

A3.2 Sample Volume

The sensitivity of the technique is directly related to the sample volume, which is normally between 2–50µl. Typical sample volumes of 10–20µl are used, the maximum aqueous sample volume is 50–100µl whilst a maximum of 20–30µl is more appropriate for organic solvents. When these larger volumes are used the improved sensitivity can be offset by the increased likelihood of the liquid sample running to the ends of the graphite tube prior to evaporating. This can lead to significant memory effects especially for involatile elements, enhanced interference effects and loss of precision.

A3.3 Automatic Sample Introduction

A3.3.1 Almost all manufacturers offer a device for automatic sample injection. It is **strongly recommended** that whenever an electrothermal atomizer is purchased, the corresponding autosampler is purchased at the same time. Manual operation of ETA devices requires injection of a sample or standards at 2–3 minute intervals on a regular basis. For good precision it is essential that samples are injected into the graphite tube on a regular time basis. This can prove very tedious for routine operation. Some Operatives find great difficulty in accurately pipetting small volumes into the restricted aperture of the graphite tube.

A3.3.2 Most automatic systems are based on injection of each sample into the graphite tube, however, one system actually nebulizes the sample into a mixing chamber and the resulting aerosol is passed into the graphite tube heated to 150°C. The aerosol then immediately dries on contact with the hot wall (see Figure A3). The sensitivity can be adjusted by varying the nebulization time.

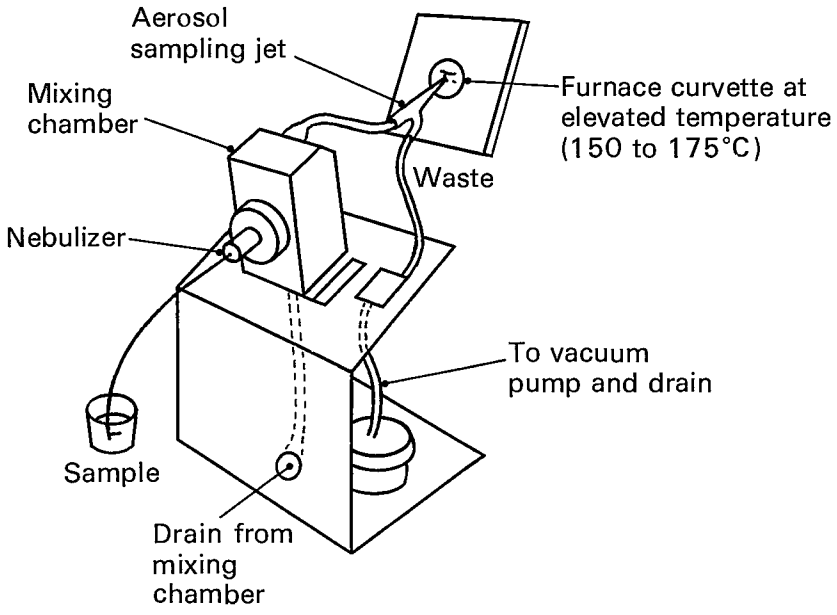
A3.3.3 The main advantages of automatic sample injection are listed below:

a) Minimal Operator involvement.
b) Very good precision, often better than 2% relative standard deviation.
c) Can be left unattended for long periods (eg over lunch, or even overnight).
d) Most units can be programmed for automatic calibration.
e) Some units allow separate addition of a matrix modifying reagent (See A3.7.5) which is automatically injected into the graphite tube directly after a sample or standard is injected.
f) Most units will automatically carry out calibration by standard addition on each sample.

A3.4 Selection of Evaporation, Dry Ash and Atomization Temperatures and Ramp Heating Rates

A3.4.1 Most commercial units allow the operator to select a temperature and time for the solvent evaporation, dry ashing and atomization stages and a rate of heating (ramp rate) to achieve these temperatures.

Figure A3 Automatic sampler based on nebulization of the aerosol on the heated graphite tube



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A3.4.2 For the solvent evaporation stage it is essential to ensure that **complete** evaporation of the solvent occurs prior to commencement of the dry ashing stage. If the heating is too rapid, spitting of the solvent and poor reproducibility will occur.

A3.4.3 The dry ashing temperature should be set to a temperature so that the maximum volatilization of the matrix occurs without significant loss of analyte. The rate of heating (ramp rate) to the selected dry ashing temperature should allow controlled decomposition and volatilization of the matrix. For samples containing significant amounts of volatile matter (eg serum) mechanical loss of sample can occur if a too rapid dry ash heating rate is used. The atomization temperature should be set to a value to volatilize and atomize both the analyte and matrix. If the matrix is not removed during the atomization stage, slow changes in sensitivity can be observed which are caused by slow build up in involatile matrix components. It is possible to utilize a low atomization temperature (eg for cadmium) and then make a high temperature firing after every 10–20 samples to remove the matrix residue. The rate of heating (ramp rate) during the atomization stage can often be quite critical and it is difficult to give specific advice for all situations. In some complex matrices (eg saline waters) a slow ramp rate can be used to separate the analyte (eg cadmium) from matrix. However for non-saline water analysis, maximum ramp rate is normally employed as this is generally regarded as minimizing chemical interference effects for this type of matrix. The use of a high (maximum) ramp rate up to the selected atomization temperature also results in an improvement in sensitivity, this is particularly marked for involatile elements such as molybdenum, titanium and vanadium. It is important that the furnace is ramped to a temperature significantly higher than the atomization temperature of the analyte to ensure uniform and reproducible atomization. For some instruments for some involatile elements, such as molybdenum and vanadium, it is necessary to operate that unit at the maximum power setting between each analytical firing to minimize memory effects. When using the L'vov platform technique (see A3.7.7), it is important to use the maximum ramp rate in order to minimize interference effects.

A3.4.4 The temperature of the graphite tube is normally sensed either by a high temperature (eg tungsten) thermocouple or a silicon diode optical detection system. For some instruments the temperature is not directly measured but is simply a function of the voltage applied to the tube. Feedback can be used to reduce temperature overshoot.

A3.5 Readout

There are three basic forms of readout, direct pen recorder, peak area and peak height readout.

A3.5.1 Recorder Readout

The instrument output is simply monitored on a conventional pen recorder and each peak height is manually measured. It is recommended that this form of readout is always used even if automatic peak area or peak height readout is used for the actual analytical measurements (see below). The pen recorder trace will give visual indication if erroneous operation occurred, (eg unstable baseline). The response time of most pen recorders is significantly greater than that for atomic absorption spectrophotometers. This results in a reduced linear range of the calibration graph for the more volatile elements compared with peak height and peak area measurements.

A3.5.2 Peak Area

The actual peak area of the transient signal is displayed and can be directly printed out. This form of measurement can minimize certain interelement effects related to the kinetics of vaporization and atomization.

A3.5.3 Peak Height

The actual maximum peak height of the transient signal is displayed and also can be directly printed out. Some atomic absorption units will simultaneously print out peak area and peak height results. It should be noted that unlike recorder readout, peak area or height readout can be directly processed by the instrument to give the actual sample analysis results and the peak displayed on a visual display unit (VDU).

A3.6 Automatic Background Correction

Non-specific background absorption is far more significant in electrothermal atomization analysis than in flame AAS. It is strongly recommended that all the routine measurements are carried out using the automatic background correction mode unless it has been conclusively proved that for a particular determination it is not necessary. Whenever a new method is being developed the background absorption signal of typical samples should be checked. If this absorption is considered significant, efforts should be made to minimize it by increasing the dry ashing temperature (see A3.4) or the addition of a matrix modifier (see A3.7.3). Most AAS units in the Water Industry use conventional automatic background correction using a hydrogen (or deuterium) arc lamp(6). However, there are some units now available that use a background correction system based on the Zeeman effect. This utilizes a magnetic field applied to the graphite tube to discriminate between atomic and background absorption. No hydrogen lamp is required. The Zeeman background correction technique(7) is more accurate when analysing samples that exhibit very significant (ie $> 0.7A$) background absorption signals (eg steels and alloys, clinical samples, saline waters etc). It is also useful for correcting structured background from matrix components, (eg the effect of iron upon selenium resulting from the presence of weekly absorbing iron atomic lines in the very close vicinity of the 196.0nm selenium line. These iron lines absorb the radiation from the deuterium background correction lamp). It also allows background correction to be applied at wavelengths above 350nm (eg Sr, Ba) where the low intensity of deuterium lamps results in poor signal to noise ratios.

An alternative technique to Zeeman background correction is the Smith-Hieftje(8) method of background correction where the analyte hollow-cathode lamp is alternately pulsed with a very high current value followed by a normal low current value. During the very high current pulse the analyte resonance line is completely self-reversed and any absorbance signal is solely due to the matrix. During the subsequent low current pulse any absorbance signal is due to both the analyte and the matrix. However, for the analysis of nonsaline waters, background absorption is not considered to be a significant problem when conventional background deuterium correction systems are used.

A3.7 Minimization of Interference Effects

A3.7.1 Chemical interference effects are far more prevalent in electrothermal atomization analysis than in conventional flame analysis. The analyst must exercise great care in the development of any new method of analysis. In general, a nitric acid matrix is preferred to a hydrochloric or sulphuric acid matrix. The degree of interference observed for given solutions is often dependent both upon the design and operation of the graphite tube atomizer. It can also be dependent upon the age (number of firings) of the graphite tube. If the atomization temperature is not sufficient to completely remove the matrix, slow changes in sensitivity as well as variations in interelement effects can sometimes be observed. It is often difficult to correlate the degree of interference with the sample matrix. For instance the interferences observed in the determination of cadmium and lead in natural waters are not directly related to calcium or magnesium concentrations. Some soft waters exhibit more significant interference (suppression of signal) than some very hard waters (9–11).

A3.7.2 There are a number of methods for overcoming or minimizing interference effects, the most commonly used methods are summarized below. It should be stressed that any proposed interference tests should be carried out at various stages (eg 10, 50 and 90%) of the expected graphite tube lifetime.

A3.7.3 Calibration by Standard Additions

Aliquots of the sample are spiked with known concentrations of the analyte and the resulting spiked samples and the original sample are then measured. The determined concentration in the sample is then obtained by graphical extrapolation of the resulting calibration graph. The major disadvantages of this technique are that at least two spiked samples must be used hence at least three measurements are required for each sample and that the calibration graph must be linear. This latter limitation can significantly reduce the usable calibration range. Some microprocessor controlled autosamplers can automatically carry out this form of calibration. Other disadvantages of standard additions are that it may not overcome all types of interference, and it may give more difficulty in correctly assessing the blank.

A3.7.4 Selective Extraction of the Determinand

Most toxic metals (eg Cd, Cu, Ni, Pb etc) can readily be extracted from natural waters after pre-treatment using a suitable extraction reagent and solvent. For instance ammonium pyrollidine dithiocarbamate/4 methylpentan–2–one (APDC/MIBK) can be used to extract a number of toxic metals from natural waters. The main matrix elements: calcium, magnesium, potassium and sodium are not extracted. A rapid semi-micro method for the determination of lead in water has recently been reported(12) using a simple APDC/MIBK extraction. The disadvantages of this type of technique are the additional operator time required to carry out the extraction technique and the increased risk of contamination. Pre-treatment such as acid digestion or UV oxidation is necessary for raw waters prior to solvent extraction in order to ensure that the metals are not bound to organic matrix components and are free to react with the extraction reagent.

A3.7.5 Matrix Modification

Addition of certain reagents to the sample solution can often significantly reduce interference effects(13–18). For instance addition of ammonium nitrate to saline water results in evolution of volatile ammonium chloride during the dry ashing step and considerably reduces both background absorption and chemical interference effects. The presence of a matrix modifier increases the volatilization temperature of the analyte. Other commonly used matrix modifiers are diammonium hydrogen phosphate, magnesium nitrate, nickel nitrate and nitric acid. References 13–18 give useful information on the use of matrix modifiers. It is essential that the matrix modifying reagents are of the highest purity with respect to the determinand element. Lanthanum salts can be considered as matrix modifiers for the determination of cadmium and lead and their use is discussed in the following section dealing with tube coatings.

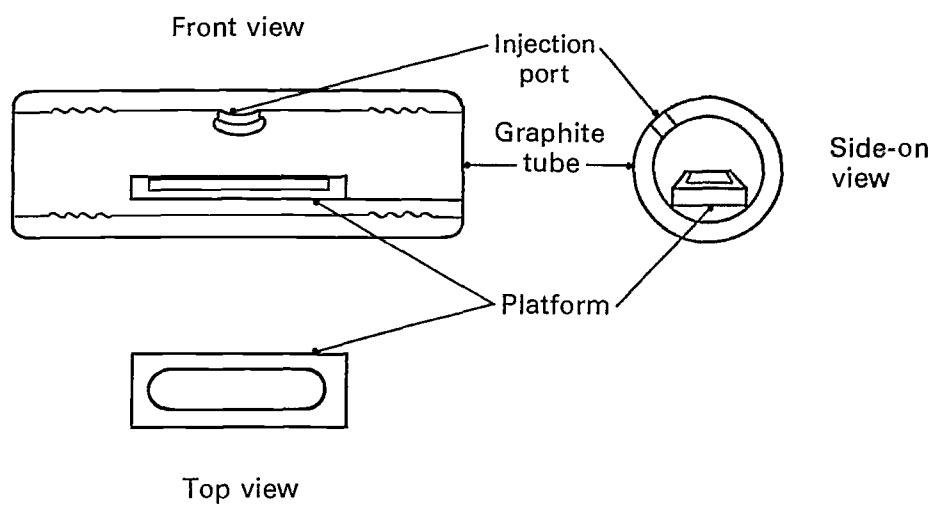
A3.7.6 Tube Coatings

Coating the graphite tube with certain involatile compounds has been found to minimize a number of interelement effects. Coatings based upon the addition of lanthanum, molybdenum, tantalum and zirconium salts have been employed for various applications (9–11, 17–20). Coatings based upon lanthanum have successfully been used for the minimization of chemical interference effects in the determination of cadmium and lead in natural waters(9–11).

A3.7.7 L'vov Platform Technique (16–18, 21–24)

When the analyte is vaporized and atomized from the graphite tube its temperature changes as it enters the gas phase which is at a significantly lower temperature than the graphite tube wall temperature. (The internal gas temperature lags behind the graphite tube wall temperature). This relatively cool and non-isothermal environment often results in significant chemical interference effects. These can often be reduced by heating the graphite tube as rapidly as possible during the atomization stage (ie using maximum ramp rate heating). However, the analyte vaporization and atomization can be delayed by placing a small pyrolytic graphite platform (known as a L'vov platform) inside the graphite tube and injecting the sample on to this platform (see Figure A4). The vaporization and atomization of the analyte is then delayed because of the time lag required for the platform to heat up. Consequently, when the platform has heated up, atomization then occurs into a much hotter and more isothermal environment thus minimizing many chemical interference effects especially when peak area measurement (see A3.5.2) is used. It is possible to utilise the L'vov

Figure A4 The L'vov platform



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platform in conjunction with a platform coating and/or a matrix modification technique(16–18, 21–24). The matrix modifier will reduce the volatility of the analyte and permit steady state temperature conditions to prevail in the graphite tube, before the analyte vaporizes from the platform. It is important that the heating rate of the graphite tube should be as rapid as possible to ensure that when the analyte vaporizes, it enters a very hot environment where reaction with matrix components is unlikely to occur. Heating rates of 1500–2000°C/s can be achieved with modern furnaces. A large number of papers (typical examples are references 16–18, 21–24) have described the powerful combination of L'vov platform, matrix modifiers and/or platform coatings for the determination of a wide variety of elements in environmental samples. In many cases calibration can be achieved using simple aqueous standards.

A WRc publication (23) has investigated the use of L'vov platforms with and without lanthanum addition for the determination of lead and cadmium in waters. The variations in the peak shapes displayed by the different methods were depicted. It was concluded that with lanthanum as a matrix modifier, cadmium and lead could be determined satisfactorily without a L'vov platform, but because the lanthanum degraded the graphite tube surface, more frequent calibration was required.

A3.8 Rate of Analysis

A typical electrothermal device can make 30–40 firings per hour and each analytical measurement is normally made at least twice as rogue results are much more likely to occur when using these devices than when using flames. For standard addition measurements each sample is spiked with at least two different determinand concentrations, and thus each analytical result requires duplicate firings from three samples (that is, the sample and the two spiked samples) and this typically takes about 9 to 12 minutes.

A4 Conclusions

The number of operating parameters in electrothermal atomization is significantly greater than in flame atomization (viz solvent, dry ashing and atomization temperatures and time settings, rate of heating during the atomization stage, nature of flow rate(s) and the purge gas(es) etc). The reproducibility of manually adding small volumes (10–50μl) of the samples and standards to the graphite heating element can vary significantly from operator to operator. However, the use of automatic sampling devices can effectively overcome this problem. With care it is possible to obtain accurate and reproducible results for a number of elements using this technique, but considerably more operator skill is required in setting up the instrumental conditions than for the conventional flame analysis. This brief introduction has clearly shown that unlike many methods based on conventional flame AAS methods it is virtually impossible to give **precise** details of a proposed electrothermal atomization method that can be guaranteed to work satisfactorily on all commercial instruments. All that can be given is general guidance with suggested operating conditions. The analyst **must** then carry out detailed optimization and interference effect studies.

The Analytical Methods Committee of the Royal Society of Chemistry has tabulated a number of features of ETA-AAS systems that should be considered when purchasing such a system(25). A method is given of scoring these features in a rational manner. This will allow potential purchasers to carry out a scientific comparison between manufacturers' instruments.

A5 References

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A6 EAAS Methods in this series

This volume contains the methods for lead and cadmium. A companion volume with methods for chromium, cobalt, copper, nickel, silver, vanadium, trace zinc and possibly other metals is in preparation.

B Determination of Cadmium and Lead in Raw and Potable Waters by Electrothermal Atomization Atomic Absorption Spectrophotometry

B1 Performance Characteristics of the Method

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

B1.1	Substance determined	All forms of cadmium and lead likely to occur in raw and potable waters.
B1.2	Type of sample	Raw and potable waters.
B1.3	Basis of method	Direct analysis by electrothermal atomization atomic absorption spectrophotometry with the addition of a lanthanium salt to acidified samples in order to minimize interference effects.
B1.4	Range of application	Up to 5μg/l cadmium Up to 100μg/l lead
B1.5	Calibration curve	Cadmium – typically linear to 5μg/l Lead – typically linear to 100μg/l (depending on instrument and operating conditions).
B1.6	Total Standard deviation * and ** B1.6.1 B1.6.2	 Cadmium see tables B1 and B3 Lead see tables B2 and B4
B1.7	Limit of detection**	0.1–0.2μg/l Cadmium 0.6–1.0μg/l Lead With 9 degrees of freedom
B1.8	Sensitivity** Cadmium Lead	5μg/l gives an absorbance of approximately 0.20 units, 100μg/l gives an absorbance of approximately 0.30 units.
B1.9	Bias*	See tables B1, B2, B3 and B4.
B1.10	Interferences * and **	See section 3 and tables B3 and B4
B1.11	Time required for analysis	The total analytical and operator times are the same (assuming manual injection) and for a batch of 10 samples are 1 hour for each metal.

*These results were obtained in an interlaboratory exercise carried out by Yorkshire Water Authority(1). The total standard deviations have approximately 9 degrees of freedom.

**These results were obtained in an interlaboratory exercise carried out by Severn Trent Water Authority(2). The total standard deviations have approximately 9 degrees of freedom.

Table B1 Cadmium

Laboratory *	Instrument	Drying temp (°C)	Ashing temp (°C)	Atomizing temp (°C)	Sample size	0.495 µg/l standard: Mean found (µg/l)	0.495 µg/l standard: Standard Deviation (µg/l)	0.495 µg/l standard: Mean bias (µg/l)	4.395 µg/l standard: Mean found (µg/l)	4.395 µg/l standard: Standard Deviation (µg/l)	4.395 µg/l standard: Mean bias (µg/l)
1	IL 451 + 655 + 254	150	600	1800	20 sec	0.511	0.079	+ 0.016	4.154	0.24	− 0.24
2	V AA − 775 + CRA 90	90	450	1450	10 µl	0.511	0.039	+ 0.016	4.820	0.25	+ 0.43
3	IL 257 + 555	110	400	2000	20 sec	0.600	0.089	+ 0.105	4.960	0.12	+ 0.57
4	PE 272 + HGA 500	120	400	2100	24 µl	0.575	0.182	+ 0.080	4.915	0.50	+ 0.52
5	V AA − 275 + CRA 90	80	450	2000	10 µl	0.550	0.055	+ 0.055	4.670	0.27	+ 0.28
6	IL 451 + 655 + 254	150	400	1800	5 sec	0.370	0.090	− 0.125	4.735	0.53	+ 0.34
7	PU SP9	115	300	1400	15 µl	0.541	0.041	+ 0.046	4.612	0.24	+ 0.22
8	IL 451 + 655 + 254	180	320	1860	10 sec	0.657	0.376	+ 0.162	4.749	0.47	+ 0.35
Laboratory **											
9	IL 157 + 555 + 254	175	400	2000	5 sec	For a 0.75 µg/l and a 3.0 µg/l standard the standard deviations ranged from 0.015 to 0.055 µg/l and 0.031 to 0.055 respectively.					
10	V AA6 + CRA 90 + ASD 53	80	450	1500	5 µl						
11	PE 603 + HGA 400 + AS 40	120	400	1850	20 µl	For a river water containing 1.5 µg/l and spiked to contain 4.5 µg/l the standard deviations ranged from 0.025 to 0.108 µg/l and 0.053 to 0.079 respectively.					

Table B2 Lead

Laboratory *	Instrument	Drying temp (°C)	Ashing temp (°C)	Atomizing temp (°C)	Sample size	Wave-length (nm)	9.90 µg/l standard: Mean found (µg/l)	9.90 µg/l standard: Standard Deviation (µg/l)	9.90 µg/l standard: Mean bias (µg/l)	87.89 µg/l standard: Mean found (µg/l)	87.89 µg/l standard: Standard Deviation (µg/l)	87.89 µg/l standard: Mean bias (µg/l)
1	IL 451 + 655 + 254	150	600	1900	20 sec	283.3	10.44	0.62	+ 0.54	90.63	4.1	+ 2.7
2	V AA − 775 + CRA 90	90	500	1700	10 µl	217.0	10.09	0.61	+ 0.19	88.55	3.2	+ 0.7
3	IL 257 + 55	110	400	2000	20 sec	283.3	9.70	0.55	− 0.20	99.80	4.2	+ 11.9
4	PE 272 + HGA 500	120	500	2100	24 µl	217.0	12.45	1.67	+ 2.55	100.70	4.7	+ 12.8
5	V AA − 275 + CRA 90	80	450	2000	10 µl	217.0	9.10	0.76	− 0.80	86.40	5.1	− 1.5
6	IL 451 + 655 + 254	175	650	2300	5 sec	217.0	9.47	1.79	− 0.43	93.25	11.9	+ 5.4
7	PU SP9	115	600	1900	12.5 µl	283.3	9.40	0.57	− 0.50	95.04	2.9	+ 7.2
8	IL 451 + 655 + 254	180	400	1780	10 sec	283.3	10.44	2.08	+ 0.54	89.01	4.6	+ 1.1
Laboratory **												
9	IL 157 + 555 + 254	175	650	2300	5 sec	217.0	For standard lead solutions containing 1.0, 5.0, 10.0, 20.0 and 40.0 µg/l the standard deviations were 0.13, 0.23, 0.46, 0.58 and 1.47 µg/l respectively. For a tap water spiked with 0.0, 2.0, 5.0, 11.0, 20.0, 50.0 and 100.0 µg/l the standard deviations were 0.24, 0.43, 0.59, 1.63, 3.00 and 4.01 respectively.					

Table B3 Cadmium

	INSTRUMENT OPERATING CONDITIONS					CADMIUM SOLUTIONS TESTED					
						0.45 µg/l standard and matrix			4.500 µg/l standard and matrix		
Laboratory *	Instrument	Drying temp (°C)	Ashing temp (°C)	Atomizing temp (°C)	Sample size	Mean found (µg/l)	Standard Deviation (µg/l)	Mean bias (µg/l)	Mean found (µg/l)	Standard Deviation (µg/l)	Mean bias (µg/l)
1	IL 451 + 655 + 254	150	600	1800	20 sec	0.984	0.136	+ 0.534	4.400	0.20	− 0.10
2	V AA − 775 + CRA 90	90	450	1450	10 µl	0.935	0.157	+ 0.485	8.198	0.83	+ 3.70
3	IL 257 + 555	110	400	2000	20 sec	1.890	0.076	+ 1.440	5.710	0.15	+ 1.21
4	PE 272 + HGA 500	120	400	2100	24 µl	0.730	0.232	+ 0.280	3.625	0.75	− 0.88
5	V AA − 275 + CRA 90	80	450	2000	10 µl	0.740	0.087	+ 0.290	3.990	0.53	− 0.62
6	IL 451 + 655 + 254	150	400	1800	5 sec	0.698	0.422	+ 0.248	6.512	1.92	+ 2.01
7	PU SP9	115	300	1400	15 µl	0.882	0.055	+ 0.432	4.633	0.24	+ 0.13
8	IL 451 + 655 + 254	180	320	1860	10 sec	0.945	0.136	+ 0.495	4.864	0.46	+ 0.36

Table B4 Lead

	INSTRUMENT OPERATING CONDITIONS						LEAD SOLUTIONS TESTED					
							9.00 µg/l standard and matrix			90.00 µg/l standard and matrix		
Laboratory *	Instrument	Drying temp (°C)	Ashing temp (°C)	Atomizing temp (°C)	Sample size	Wave-length (nm)	Mean found (µg/l)	Standard Deviation (µg/l)	Mean bias (µg/l)	Mean found (µg/l)	Standard Deviation (µg/l)	Mean bias (µg/l)
1	IL 451 + 655 + 254	150	600	1900	20 sec	283.3	11.18	1.35	+ 2.18	95.56	8.7	+ 5.6
2	V AA − 775 + CRA 90	90	500	1700	10 µl	217.0	8.61	0.74	− 0.39	80.81	3.4	− 9.2
3	IL 257 + 555	110	400	2000	20 sec	283.3	7.50	0.55	− 1.50	82.60	2.2	− 7.4
4	PE 272 + HGA 500	120	500	2100	24 µl	217.0	8.20	1.82	− 0.80	73.20	8.7	− 16.8
5	V AA − 275 + CRA 90	80	450	2000	10 µl	217.0	6.30	0.71	− 2.70	64.70	5.2	− 25.3
6	IL 451 + 655 + 254	175	650	2300	5 sec	217.0	8.90	3.62	− 0.10	84.32	29.3	− 5.7
7	PU SP9	115	600	1900	12.5 µl	283.3	11.14	1.09	+ 2.14	99.56	2.9	+ 9.6
8	IL 451 + 655 + 254	180	400	1780	10 sec	283.3	7.67	1.36	− 1.33	71.15	5.0	− 18.9

NOTES

General

These results are illustrative of the performance achieved with various instruments in routine use in the participating laboratories; different results may be obtained using the same model and/or make of instrument in different laboratories with different operators. Therefore the results should not be interpreted to mean that any make or model is superior to another. The operating conditions are provided for guidance only and are examples of conditions which have been employed. Analysts must optimize the operating conditions to obtain the most satisfactory performance for their particular instruments.

B2 Principle

Cadmium and lead in raw and potable waters are determined directly in acidified aqueous samples by electrothermal atomization atomic absorption spectrophotometry. A lanthanum salt is added to the samples before analysis in order to minimize the negative bias due to suppressive interference effects.

Potable waters and filtered raw waters are analysed directly without pre-treatment. When total cadmium or total lead are required on samples containing suspended matter a pre-treatment step is necessary to solubilize the metals.

B3 Interferences

With the method used as described, no specific interferences have been found. Lead and Cadmium recoveries (expressed as mean bias) from a matrix containing 0.68 mg/l NO_3^-, 0.136 mg/l NH_3, 23.0 mg/l Cl^-, 45.8 mg/l $SO_4^=$, 12.7 mg/l Ca, 1.7 mg/l Mg, Alkalinity = 389 mg/l $CaCO_3$ are given in tables B3 and B4. The results indicate considerable variation in matrix effects between different instruments in different laboratories; some of these recoveries are unsatisfactory. Laboratories using other instruments are advised to check their own recoveries. Lead(2) added to a wide range of sample types has been satisfactorily recovered (see table B5).

Table B5

Sample	Concentration of major ions present (mg/l) Ca^{++}	Mg^{++}	Na^+	K^+	Cl^-	$SO_4^=$	lead concn. µg/l	%Recovery of 50% µg/l lead spike (a)
A River	33	5	13	5	18	48	2.8	101
B River	68	14	32	3	44	88	1.0	107
C River	100	24	47	7	63	187	< 1.0	106
D River	173	16	93	36	98	460	2.2	112
E T Effluent	560	24	109	8	1120	126	13.3	101
F S Effluent	54	6	96	8	120	154	2.1	116
G Borehole	118	19	19	14	36	86	< 1.0	100
H Borehole	148	36	20	6	31	257	< 1.0	99
I Borehole	210	48	210	15	267	600	< 1.0	96
J Borehole	700	63	360	9	590	850	< 1.0	107
K Borehole	465	90	760	8	1150	1150	< 1.0	101

(a) If other substances did not interfere the 95% confidence limits are estimated to be approximately 88–112% for the recovery of the spiked lead. The recoveries quoted are the means of duplicate analyses of the unspiked and spiked samples.

B4 Hazards

The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away. Avoid looking at the glare from the atomization stage as prolonged viewing could possibly cause cataracts.

B5 Reagents

All reagents and standard solutions must be stored in polyethylene bottles unless otherwise stated.

B5.1 Water

The water used for blank determinations and for preparing reagents and standard solutions should have a cadmium and lead content that is negligible compared with the smallest concentrations to be determined in the samples. Deionized water or water distilled from an all glass apparatus should be suitable.

B5.2 Nitric Acid (d_{20} 1.42), atomic spectroscopy grade

B5.3 10% V/V Nitric Acid

Dilute 100 ± 1ml of nitric acid (d_{20} 1.42), atomic spectroscopy grade, with water to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

B5.4 10% M/V Lanthanum Solution

Dissolve either 26.6 ± 0.1g of lanthanum chloride ($LaCl_3.7H_2O$) or 31.2 ± 0.1g of lanthanum nitrate ($La(NO_3)_3.6H_2O$) in water and dilute to 100 ml in a measuring

cylinder. Store in a polyethylene bottle. High purity grades of lanthanum salts must be used. For some instruments only lanthanum nitrate has been found satisfactory.

B5.5 0.5% M/V Lanthanum Solution (tube conditioning solution)

Dilute 5.0 ± 0.1 ml of solution B5.4 with water to 200 ml in a measuring cylinder. Store in a polyethylene bottle. (See Section B6.2).

B5.6 Standard Cadmium Solutions

B5.6.1 Solution A 1 ml is equivalent to 100 μg Cd.

Weight 100.0 ± 0.5 mg of cadmium wire (greater than 99.9% purity) and dissove with gentle heating in a mixture of 50.0 ± 0.5 ml of nitric acid (d_{20} 1.42) atomic spectroscopy grade and approximately 50 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.

B5.6.2 Solution B 1 ml is equivalent to 0.1 μg Cd

Dilute 1.00 ± 0.01 ml of solution A with water, to 1 litre in a calibrated flask. This solution should be freshly prepared before use.

B5.7 Standard Lead Solutions

B5.7.1 Solution A 1 ml is equivalent to 1 mg Pb

Weigh 0.500 ± 0.005 g of lead wire (greater than 99.9% purity) and dissolve with gentle heating in a mixture of 25.0 ± 0.5 ml of nitric acid (d_{20} 1.42) atomic spectroscopy grade, and approximately 25 ml of water. Quantitatively transfer the solution to a 500 ml calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months. Alternatively use a commercially available standard solution.

B5.7.2 Solution B 1 ml is equivalent to 2.0 μg Pb

Dilute 2.00 ± 0.01 ml of solution A with water to 1 litre in a calibrated flask. This solution should be freshly prepared before use.

B6 Apparatus

B6.1 An atomic absorption spectrophotometer equipped with an electrothermal atomizer and cadmium and lead hollow-cathode lamps. Simultaneous background correction facility using a hydrogen or deuterium hollow-cathode or arc lamp is necessary. A chart recorder or visual display unit is a desirable form of read out since it will give a visual indication if erroneous operation has occurred even though peak height or peak area is actually used for calculating the result.

B6.2 Atomizer tubes, non-pyrolytically coated, should be pre-conditioned before use by making at least five replicate injections of a 0.5% lanthanum solution and heating through the complete operating cycle. Check that the tube has been conditioned satisfactorily by ensuring that replicate injections of an analytical quality control standard gives stable sensitivity and constant recovery using spiked samples (see Section B11).

It may also be possible to utilise the L'vov platform technique for this determination (See A3.7.7). The user would have to check the performance characteristics after making suitable adjustments to the evaporation, dry ash and atomization temperatures to compensate for the different heating characteristics of a platform. Some useful information on this topic is given in Section A, references 14, 23 and 24. References 14 and 24 recommend matrix modification reagents based on phosphate rather than lanthanum.

B6.3 Cleanliness — Cleanliness is absolutely essential for this procedure. If possible a separate room with a clean environment should be reserved solely for electrothermal atomization work. Apparatus must also be reserved solely for these determinations and all new glass and polyethylene ware must be thoroughly cleaned before use by filling or soaking in 10% V/V nitric acid for at least two days. Rinse thoroughly with water before use. It is advisable to soak all glass and polyethylene ware in 10% V/V nitric acid routinely when not in use. Merely rinsing in nitric acid before use may not be sufficient.

B7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in section B6.3, add 1.00 ± 0.05 ml of nitric acid (d_{20} 1.42) atomic spectroscopy grade per 100 ml of sample to be collected and then collect the sample. The acidification minimizes the adsorption of cadmium and lead onto the walls of the bottle and this concentration of nitric acid (ie 1% V/V) in samples has been found to be the optimum level for the analysis.

B8 Sample Pretreatment

No pretreatment is necessary for potable waters and filtered raw waters and the analysis of such samples should start at step B9.2 of the analytical procedure. For samples containing suspended matter for which total cadmium and total lead analyses are required a pretreatment step is necessary to solubilize the metals. The pretreatment procedure given in Step B9.1 is a balance between ensuring adequate dissolution of the metals and the potential problems of contamination if a more severe digestion procedure is employed. The analyst must check to ensure that the recommended pretreatment procedure is satisfactory for his particular samples.

B9 Analytical Procedure

Step	Procedure	Notes
	Analysis of Samples	
	Pretreatment stage (notes a and b)	
B9.1	Place the polyethylene bottle containing the sample in an oven at 80 ± 3°C for 2.0 ± 0.1 hours and allow to cool. Alternatively add 100 ± 1 ml of the sample to a 150 ml borosilicate glass beaker. Cover the beaker with a watch glass and bring to the boil on a hot plate. No reduction in volume should occur. Allow the solution to cool to ambient temperature.	(a) Ensure that the nitric acid concentration is 1% V/V in the sample. (b) If pretreatment is not required start at step B9.2.
B9.2	Fill a 100 ml calibrated flask or measuring cylinder (borosilicate or polyethylene) to the mark with sample or pretreated sample. Add 0.50 ± 0.05 ml of 10% lanthanum solution and mix well (note c).	(c) If the sample is above the concentration range of the method, the appropriate volume of sample should be diluted to 100 ml. Ensure that the diluted sample remains 1% V/V in nitric acid.
B9.3	Proceed to the electrothermal atomization atomic absorption stage, step B9.9.	

Step	Procedure	Notes
	Blank Determination	
B9.4	A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples.	
B9.5	Using 100 ± 1 ml of water instead of sample proceed with steps B9.1 to B9.3 inclusive if the pretreatment stage was used for samples. If not, carry out only steps B9.2 and B9.3.	
	Calibration Standards	
B9.6	A calibration standard must be run with each batch (eg 3 to 5 samples) of determinations using the same batch of reagents as for the samples (see Section B10). To a 100 ml calibrated flask (borosilicate or polyethylene) add from a pipette 2.50 ml of standard cadmium solution B and 10.0 ± 0.2 ml of 10% V/V nitric acid, and dilute with water to the mark. This corresponds to a cadmium concentration of 25 μg/litre.	
B9.7	Repeat step B9.6 using 2.50 ml of standard lead solution B. This corresponds to a lead concentration of 50 μg/litre.	
B9.8	If the pretreatment stage was used for the samples, carry out steps B9.1 to B9.3, inclusive. If not, carry out only steps B9.2 and B9.3.	
	Electrothermal Atomiztion Atomic Absorption Spectrophotometry	
B9.9	Set up the instrument according to the manufacturer's instructions for the determination of cadmium and lead by electrothermal atomization using automatic background correction (note d). Each new tube should be conditioned with lanthanum as described in Section B6.2.	(d) To obtain satisfactory performance, it is often necessary for the analyst to optimize the atomization cycle to suit his particular instrument. Operating conditions that have been used successfully are given in Table 1 for a variety of instruments.
B9.10	Using either a manual or automated system as required, inject an appropriate volume of the calibration standard and ensure that the instrument gives a satisfactory response (note e).	(e) An appropriate volume is usually in the range 5–20 μl depending on the particular instrument employed. The same volume should be used for all subsequent samples, standards and blanks.
B9.11	Inject the blank and re-inject the calibration standard (note f). Let the response of the blank and calibration standard be B_1 and C_1 respectively.	(f) It is recommended that all injections are carried out in duplicate. If the agreement is not satisfactory the determination should be repeated.
B9.12	Inject a standard, a spiked sample and an unspiked sample (see Section B11.4) and measure the responses (notes f and g).	(g) The recovery of the spike addition should meet the criteria given in Section B11. If it does not the cause should be investigated and overcome before proceeding with the analysis of samples.

Step	Procedure	Notes

B9.13 Inject the samples and measure the responses (note f). Let the mean response of the sample be S.

B9.14 To check for any instrumental drift, at the end of a batch (eg 3 to 5 samples) inject both the blank and the calibration standard and measure the response, B_2 and C_2 respectively.

B9.15 If B_1 and B_2 and also C_1 and C_2 are in satisfactory agreement calculate the means $\bar{B}$ and $\bar{C}$.

Calculation of Results

B9.16 Calculate the concentration of cadmium and lead in the sample as follows:

$$\text{Cadmium} = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 25 \ \mu g/l$$

$$\text{Lead} = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 50 \ \mu g/l$$

where $\bar{C} = \frac{C_1 + C_2}{2}$

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

This calculation assumes a linear calibration curve. Linearity must be checked (see Section B10).

B9.17 If dilution was necessary in step B9.2 and Vml of sample was diluted to 100 ml, the calculation becomes

$$\text{Cadmium} = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 25 \times \frac{100}{V} \ \mu g/l$$

$$\text{Lead} = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 50 \times \frac{100}{V} \ \mu g/l$$

B10 Checking the Linearity of the Calibration Curve

The procedure given in this section must be carried out before the analysis of each batch of samples.

B10.1 Cadmium

To a series of 100 ml calibrated flasks (borosilicate or polyethylene) add 1.00 ± 0.05 ml of nitric acid (d_{20} 1.42). Add by pipette to these flasks 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of standard cadmium solution B and dilute with water to the mark, ensuring that the diluted standard contains 1% V/V nitric acid. These solutions correspond to cadmium concentrations of 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 µg/litres respectively.

To each flask add 0.50 ± 0.05 ml of 10% lanthanum solution and mix well. Carry out steps B9.9 to B9.15 inclusive and plot the response agains µg/l cadmium.

B10.2 Lead

To a series of 100 ml calibrated flasks (borosilicate or polyethylene) add 1.00 ± 0.05 ml of nitric acid (d_{20} 1.42). Add by pipette to these flasks 0.0, 2.0, 2.0, 3.0, 4.0 and 5.0 ml of standard lead solution B and dilute with water to the mark, ensuring that the diluted standard contains 1% V/V nitric acid. These solutions correspond to lead concentrations of 0.0, 20.0, 40.0, 60.0, 80.0 and 100.0 µg/litre respectively.

To each flask add 0.50 ± 0.05 ml of 10% lanthanum solution and mix well. Carry out steps B9.9 to B9.15 inclusive and plot the response against µg/l lead.

B10.3 The calibration graphs of absorbance against concentration are normally linear* to 5 µg/l cadmium and 100 µg/l lead; 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 the calibration standard in steps B9.6 and B9.7 is not appropriate, nor is the range given in section B1.4. In such a case the calibration standard chosen for steps B9.6 and B9.7 should be the highest concentration on the linear portion of the calibration curve and the concentration range of the method shoud be adjusted accordingly.

**Note:* Some modern instruments have curve correction facilities and with them it is satisfactory to operate with a non-linear response provided the degree of curvature is not excessive. Analysts using such instruments should check the degree of curvature.

B11 Checking the Accuracy of Analytical Results

B11.1 Electrothermal Atomization Atomic Absorption Spectrophotometry, using commercially available furnaces, is often subject to large interference effects unless special procedures are employed. Moreover, such interference may vary from atomizer to atomizer, because of differences in basic design (for example, physical dimensions and heating rates).

B11.2 In the methods described in this booklet, the interference effects to which the technique is subject are reduced by adding lanthanum to the samples. Although the effectiveness of lanthanum in reducing interferences in the determination of lead and cadmium in water has been shown in several studies, it does not eliminate such effects completely, the mechanism of its action is by no means wholly understood and its effectiveness may vary with the type of furnace used. For these reasons, it is recommended that analysts wishing to use the methods given in this booklet exercise particular caution, both in establishing them with their own instrumentation and, subsequently, in applying them routinely. The following approach is recommended.

B11.3 Establishment of the method

B11.3.1 The extent to which the exact conditions of graphite furnace operation described can be reproduced on the user's instrumentation will depend upon the characteristics of the particular furnace system. It should be noted that the same choice of heating rates, for example, may not be available even on closely-related furnaces of the same manufacturer, and furnaces from different manufacturers may often show greater differences. Although the trend towards greater flexibility of heating programmes, evident with the more recent furnaces, may reduce the difficulty of duplicating particular conditions, the user should exercise great care in matching (as closely as possible) the heating conditions and temperatures described. In doing so, analysts should, of course, follow the conditions which have been employed for the furnace which most closely resembles their own. Only if the particular characteristics of his own equipment dictate otherwise, or if unsatisfactory performance is shown by the preliminary tests, should there be a marked departure from the conditions described in the method, and special care should be taken if this proves necessary.

B11.3.2 After suitable furnace conditions have been established, the calibration procedure described in the method should be carried through on at least two separate occasions. If curve straightening facilities are to be employed, their operation should be carefully checked. If the results of these checks are satisfactory, assessment of random errors can proceed, together with recovery testing.

B11.3.3 The recommended approach to such assessment has been described elsewhere(3)(4), and these references should be consulted for details. As a minimum, it is recommended that the following should be analysed as samples, in each of a number of batches:

i. A blank

ii. Two standard solutions at concentrations near the upper and lower limits of the range of interest.

iii. A real sample, both unspiked and spiked.

The number of batches, and of replicates in each batch, should be selected appropriately, (see references 3 and 4). The blank should always be determined at least in duplicate to allow an estimate of the limit of detection to be obtained. The real sample selected should be one, of the type to be analysed routinely, which is expected to be particularly susceptible to interferences (eg a sample with a high matrix concentration). If possible, the unspiked sample should contain only a negligible concentration of the determinand; spiking to about the mid-point of the range of interest will then be appropriate.

B11.3.4 If these precision and recovery tests give satisfactory results, further checks on bias should be undertaken. As a minimum, it is recommended that further recovery tests be undertaken using samples typical of those to be examined must, of course, be decided by the analyst in the light of all the information available to him. The following factors will obviously be important:

(a) The diversity of sample types to be analysed routinely.

(b) The degree of similarity between the instrumentation employed and that used to obtain the performance data given here.

Again, the unspiked samples should be obtained with a low determinand concentration, if possible.

B11.3.5 If these further tests do not disclose the existence of important bias, the method can be put into routine operation. However, recovery tests cannot show the existence of bias which is independent of determinand concentration, and interference tests are also recommended if effort is available. Guidance on the conduct of both recovery and interference tests has been given elsewhere(4). It is recommended that tests of major ionic components be made, both individually and in combination.

B11.4 Routine analytical quality control

Once the method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of 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 both a standard solution *and* a spiked and unspiked sample shoud be analysed at the same time and in the same way as normal samples (see section B9). The results should then be plotted on quality control charts in order to facilitate detection of deterioration of accuracy. Guidance on the use of such control systems has been given elsewhere(3)(2), and these references should be consulted for details. The sample used for the routine recovery test should again be one likely to be susceptible to interferences.

B12 References

(1) Department of the Environment File SW/646/161, Paper SCA/WO/ETA/6.

(2) Burtenshaw M P, Gelsthorpe D and Wheatstone K C, *Analyst* 1981 **106**, 23–31.

(3) *General principles of sampling and accuracy of results 1980*, Methods for the Examination of Waters and Associated Materials HMSO.

(4) Wilson A L and Cheesman R V, Water Research Centre, *Technical Report TR66* Medmenham 1978.

C Lead and Cadmium in Potable Waters by Atomic Absorption Spectrophotometry (Dithiocarbamate — MIBK Extraction Method)

(These are the 1976 methods reissued)

Note: Throughout these methods lead and cadmium are expressed as the elements (Pb and Cd).

C1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see another publication in this series(5).)

C1.1 Substances determined

All forms of lead and cadmium likely to occur in potable waters (see Sections C2 and C8).

C1.2 Type of sample

Potable and similar clean fresh water.

C1.3 Basis of the method

Extraction of pyrrolidine dithiocarbamato-lead and -cadmium into 4-methylpentan-2-one followed by atomic absorption spectrophotometry.

C1.4 Range of application (a)

Up to 100 µg/l lead
Up to 10 µg/l cadmium (see Section C12)

C1.5 Calibration curve

Up to 100 µg/l lead
Up to 10 µg/l cadmium (see Section C11)

C1.6 Standard deviation

Lead concentration (µg/l)	Standard deviation (µg/l)
0.0(c)	0.3–2.1(b)
50.0(c)	0.9–3.2(b)
50.0(c)	0.9–3.8(b)
100.0(d)	3.0 (a)

Cadmium concentration (µg/l)	Standard deviation* (µg/l)
0.0	0.07(c)
10.0	0.30(c)

(Each estimate of standard deviation has approximately 8 degrees of freedom.)

C1.7 Limit of detection (b)

1.0–6.0 μg/l lead. (Each estimate of limit of detection has either 50 or 10 degrees of freedom).

0.3 μg/l cadmium (with 10 degrees of freedom).

C1.8 Sensitivity (a)

100 μg/l lead gives an absorbance of approximately 0.07.

10 μg/l cadmium gives an absorbance of approximately 0.10.

C1.9 Bias (b)

Average bias for lead + 2.6 μg/l on analysing 3 tap waters of lead concentrations ranging between 50.0 and 90.0 μg/l.

Not known for cadmium.

C1.10 Interferences

For lead see Section C3.
For Cadmium, 5 mg/l Zinc may interfere, see Section C3.

C1.11 Time required for analysis (a)

The total analytical and operator times are the same. Typical times for 1 and 10 samples are approximately 2.25 and 3.0 hours respectively excluding any pretreatment time (see also step C9.7).

(a) These data were obtained at the Water Research Centre (Medmenham Laboratory)(1) using a procedure essentially the same as this method and a single beam atomic absorption spectrophotometer.

(b) These data were obtained from an interlaboratory calibration exercise in which 11 laboratories took part(2) and from tests at the Water Research Centre (Medmenham Laboratory). The range of standard deviations between individual participating laboratories has been given.

(c) Deionized water spiked with the stated lead or cadmium concentration.

(d) Tap water spiked with the stated lead concentration; the unspiked tap water contained between 0.0 and 7.0 μg/l.

(h) *These data were obtained using this method without the pretreatment procedure.

C2 Principle

C2.1 The method described is based on experimental work carried out by the Water Research Centre (Medmenham Laboratory)(1). Lead and cadmium are extracted together quantitatively, and both elements may be determined in the same solvent extract.

C2.2 Some samples may require pretreatment (see Section C8) by boiling with nitric acid to convert the lead and cadmium to forms capable of reacting with ammonium pyrrolidine dithiocarbamate (APDC). The lead and cadmium chelates formed by the reaction with APDC are extracted into 4-methylpentan-2-one (methyl isobutyl ketone — MIBK) and the amount of lead or cadmium in the extract determined by atomic absorption spectrophotometry at the appropriate wave length by aspirating directly into the flame.

C3 Interference

Substances usually present in potable waters at their normal concentrations do not cause interference. Lead added to samples has been satisfactorily recovered(3). However, low recoveries of cadmium have been reported(4) when zinc is present at a concentration greater than 5 mg/l. This effect can be overcome by dilution of the sample prior to carrying out the procedure in Section C9, so that the concentration of zinc is reduced below 5 mg/l. This results in some loss of sensitivity. Calcium and Magnesium, which occur in very hard waters, can, if present in considerable amounts, affect the flame ionization of other elements and so cause repression of the signal giving a negative bias. If the solvent extraction step is omitted, apparent losses of up to 30% of the lead and cadmium present have been reported with very hard waters.

C4 Hazards

The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away. One of the reagents, 4-methylpentan-2-one (MIBK) is flammable and has a harmful vapour (see Section C5.5). It is irritating to the eye and mucous membranes and is narcotic in high concentrations. It must not be pipetted by mouth.

C5 Reagents

All reagents and standard solutions should be kept in polyethylene bottles unless otherwise stated (see Section C6.3). Analytical reagent grade chemicals are suitable unless otherwise stated.

C5.1 Water

the water used for blank determinations and for preparing reagent and standard solutions should have a cadmium content that is negligible compared with the smallest concentration to be determined in the samples (see Section C13.2). Deionized water or water distilled from an all glass apparatus is suitable.

C5.2 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.

C5.2.1 3% V/V Hydrochloric Acid

Dilute 6.0 ± 0.1 ml of 50% V/V hydrochloric acid with water to 100 ml in a measuring cylinder. Store in a polyethylene bottle.

C5.3 Nitric Acid (d_{20} 1.42)

C5.3.1 10%V/V Nitric acid

Dilute 100 ± 1 ml of nitric acid (d_{20} 1.42) with water to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

C5.4 1%m/V Ammonium pyrrolidine dithiocarbamate (APDC)

Dissolve 1.0 ± 0.1 g of APDC in water and dilute with water to 100 ml in a measuring cylinder. This solution should be freshly prepared before use. Mix thoroughly before use.

C5.5 4-Methylpentan-2-one (MIBK)

This reagent is hazardous (see Section C4). It is flammable and has a harmful vapour. A special grade of this solvent for atomic absorption spectrophotometry is preferable. Alternatively other grades may be purified by distillation in an all borosilicate glass apparatus. Adequate precautions must be taken during distillation including carrying it out over a distillation tray. MIBK should be stored in a glass bottle.

C5.6 10% m/V Sodium hydroxide

Dissolve 10.0 ± 0.1 g of sodium hydroxide in water in a polyethylene beaker, cool and dilute with water to 100 ml in a polyethylene measuring cylinder. Store in a polyethylene bottle.

C5.7 0.1% m/V Bromophenol blue solution

Dissolve 0.10 ± 0.01 g of bromophenol blue in 100 ± 1 ml of 50% V/V aqueous ethanol.

C5.8 Standard solutions:

Lead

C5.8.1 Solution A 1 ml is equivalent to 1 mg Pb

Weigh 1.000 ± 0.005 g of 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.

C5.8.2 Solution B 1 ml is equivalent to 2 μg Pb

Dilute 2.00 ± 0.01 ml of solution A with water to 1 litre in a calibrated flask. This solution should be freshly prepared before use.

Cadmium

C5.8.3 Solution A 1 ml is equivalent to 100 μg Cd

Weigh 100.0 ± 0.5 mg 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.

C5.8.4 Soltuion B 1 ml is equivalent to 0.2 μg Cd

Dilute 2.00 ± 0.01 ml of solution A with water to 1 litre in a calibrated flask. This solution should be freshly prepared before use.

C6 Apparatus

C6.1 An atomic absorption spectrophotometer equipped for an air/acetylene flame and with lead and cadmium hollow cathode lamps. A chart recorder is a desirable form of read out. Scale expansion should be used to ensure that adequate recorder response is achieved with the highest calibration standard used (see B6.1).

C6.2 Special apparatus

Glass tubes 20 × 50 mm for the collection of the organic phases after the solvent extraction of the samples. These tubes should be fitted with snap-on polyethylene lids.
400-ml graduated borosilicate glass beakers.
250-ml glass separating funnels fitted with ground glass stoppers and taps.

C6.3 Cleanliness

Cleanliness is essential for this determination. If possible, apparatus should be reserved solely for these determinations: all residual lead and cadmium from previous determinations must be removed. Clean all new glass and polyethylene ware by filling

with or soaking in 10% V/V nitric acid for 2 days. Rinse thoroughly with water. Thereafter a thorough rinse in 10% V/V nitric acid followed by a thorough rinse with water after each determination should suffice.

C7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section C6.3, add 2.00 ± 0.05 ml of 50% V/V hydrochloric acid per litre of sample to be collected and then collect the sample. The acidification minimizes the absorption of lead and cadmium onto the walls of the bottle. Under certain circumstances (eg sampling by a householder) it may be necessary to modify the sampling procedure. When it is known that pretreatment will not be necessary (see Section C8) it is satisfactory to add to the empty bottle sufficient 50% V/V hydrochloric acid to bring the collected sample to pH 2.5 ± 0.3. It is then necessary to start the analytical procedure at step C9.5 by placing 200 ± 1 ml of the sample in the separating funnel.
Alternatively see B7.

C8 Sample Pretreatment

Samples containing suspended and/or colloidal material may require pretreatment to convert lead and cadmium to an extractable form. A few organic lead and cadmium compounds may not be converted by this pretreatment procedure. Experience will indicate to analyst whether pretreatment is necessary for certain waters. The pretreatent procedure is given in steps C9.1 and C9.2.

C9 Analytical Procedure

READ SECTION C4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
	Analysis of samples	
	Pretreatment stage (note a)	
C9.1	Add 200 ± 1 ml of the sample (note b) to a 400-ml graduated borosilicate glass beaker. Add 1.0 ± 0.1 ml of nitric acid (d_{20} 1.42). Cover the beaker with a watch glass and simmer on a hot plate until the solution volume is reduced to 20 ± 5 ml (note c).	(a) If pretreatment is not required (see Section C8), add 200 ± 1 ml of sample to a 400-ml graduate borosilicate glass beaker and start at step C9.3, but omit step C9.4. This will result in a volume slightly greater than 200 ml, but it will not significantly affect the final result. (b) See Section C12 for the concentration range of the method. If cadmium is being determined, the zinc concentration in the sample must be less than 5 mg/1; if it is higher, the sample must be diluted accordingly and an appropriate allowance made in the calculation of the result. (c) Great care must be taken during this step to minimize contamination (see Section C13).
C9.2	Cautiously wash down the watch glass and the sides of the beaker with water until the volume in the beaker is 150 ± 5 ml. Replace the watch glass and allow the solution to cool to ambient temperature.	

Step	Procedure	Notes
	Solvent extraction stage	
C9.3	Add 3 drops of 0.1% m/V bromophenol blue solution and, whilst swirling, slowly add 10% m/V sodium hydroxide until a blue colour persists. Whilst swirling, add 3% V/V hydrochloric acid dropwise until the blue colour is just discharged. Then add 2.0 ± 0.1 ml of 3% V/V hydrochloric acid (note d).	(d) Experience shows that the pH value at the end of step 9.3 should be 2.5 ± 0.3. Very occasionally solutions may require readjustments to this value.
C9.4	Transfer the solution to a measuring cylinder and dilute the water to 200 ± 1 ml (note e).	(e) The aqueous volume affects the final result. A constant 200 ml is therefore used.
C9.5	Transfer the solution to a separating funnel. Add 4.00 ± 0.05 ml of APDC solution and shake to mix. Add 10.00 ± 0.05 ml of MIBK (notes f and g) and stopper the funnel.	(f) MIBK has a harmful vapour and must not be pipetted by mouth. (g) If both elements are to be determined on the same aliquot of the sample, up to 25 ml of MIBK may be used throughout. However, there will be considerable loss of sensitivity and possibly also of precision.
C9.6	Shake the funnel vigorously for 2 min ± 15 s. Allow to stand for 5 min ± 30 s and then separate and discard the aqueous phase.	
C9.7	Run the organic phase into a sample tube and fit the lid (note h). Complete the atomic absorption stage during the same working day.	(h) All samples, blanks and standards should be processed to this stage before proceeding to the atomic absorption stage.
	Blank determination	
C9.8	A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples. To a 400-ml graduated borosilicate glass beaker add 0.40 ± 0.05 ml of 50% V/V hydrochloric acid and 200 ± 1 ml of water.	
C9.9	If the pretreatment stage was used for the samples, carry out step C9.1 to C9.7 inclusive. If not, carry out stepts C9.3 and C9.7 inclusive.	
	Calibration standards	
C9.10	Duplicate calibration standards must be run with each batch (eg up to 10 samples) of determinations (see Section C13.4). To a 500-ml calibrated flask add 1.00 ± 0.05 ml of 50% V/V hydrochloric acid. Pipette into the flask 25.0 ml of standard solution B for the appropriate metal, (note i), dilute with water to the mark and mix well. Place 200 ± 1 ml of this solution in a 400-ml graduated borosilicate glass beaker.	(i) Mixed lead and cadmium standards may be made up, by double addition, if so desired. They must be carefully labelled to avoid confusion.
C9.11	If the pretreatment stage was used for the samples, carry out steps C9.1 to C9.7 inclusive. If not, carry out steps C9.3 and C9.5 to C9.7 inclusive.	

Step	Procedure	Notes
	Atomic absorption stage	
C9.12	Set up the instrument according to the manufacturer's instructions for aspirating organic solvents into an air-acetylene flame. The wavelength required for lead is 283.3 nm. The wavelength required for cadmium is 228.8 nm.	
C9.13	Aspirate pure MIBK and adjust the zero. Aspirate one of the calibration standards (notes j and k) and adjust the instrument to give a suitable response, eg approximately 80% of full scale deflection.	(j) Keep the aspiration tube above the bottom of the sample tube to avoid aspiration of water which may have collected in the bottom of the sample tube. (k) Do not aspirate more than one-third of the organic phase at this stage as it is required for two further aspirations.
C9.14	Aspirate pure MIBK and readjust the zero if necessary. Re-aspirate both the calibration standards with an aspiration of pure MIBK after each and measure the maximum instrument responses C_1 and C_2 (eg peak height).	
C9.15	Aspirate the blank (note j) and then pure MIBK and measure the maximum instrument response B_1. Aspirate the samples (note j) with an aspiration of pure MIBK after each. Measure the maximum instrument response of the sample, S.	
C9.16	To check for any instrument drift aspirate both calibration standards and the blank with an aspiration of pure MIBK after each and measure the maximum instrument responses (eg peak height) C_3, C_4, and B_2 respectively. If C_1, C_2 and C_4 and also B_1 and B_2 are in satisfactory agreement calculate the means $\bar{C}$ and $\bar{B}$.	
	Calculation of results (see Section C12)	
C9.17	Calculate the concentration, A, of lead in the sample from $A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 100\ \mu g/l$ Where $\bar{C} = \frac{C_1 + C_2 + C_3 + C_4}{4}$ $\bar{B} = \frac{B_1 + B_2}{2}$ Calculate the concentration, A of cadmium in the sample form $A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 10\ \mu g/l$ Where $\bar{C} = \frac{C_1 + C_2 + C_3 + C_4}{4}$ $\bar{B} = \frac{B_1 + B_2}{2}$ The calculations assume linear calibration curves. Linearity must be checked (see Section C11).	

C10 Measurement of Maximum Instrument Responses

The Maximum instrument responses for samples, standards and blanks are measured with respect to the response of pure MIBK aspirated on either side. The following example is for the measurement of peak height when a chart recorder is in use.

Draw a line on the chart through the traces for the pure MIBK bracketing the peak height to be measured. Draw a line through the trace corresponding to the equilibrium response of that peak height, and measure the perpendicular separation of the two constructed lines using a ruler. When the recorder traces show short-term variations it is suggested that the lines be drawn through the visually estimated mid-points of the equilibrium portions of the traces.

C11 Checking the Linearity of the Calibration Curve

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.

To each of a series of 500-ml calibrated flasks add 1.00 ± 0.05 ml of 50% V/V hydrochloric acid. Pipette respectively to these flasks 0.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml of standard solution B for the appropriate metal and dilute with water to the mark. These flasks contain respectively 0, 20, 40, 60, 80 and 100 μg/l lead, or 0, 2, 4, 6, 8 and 10 μg/l cadmium. Place 200 ± 1 ml of these solutions in a series of 400-ml graduated borosilicate glass beakers and carry out the procedure given in steps C9.4, C9.5 to C9.7 inclusive and steps C9.12 to C9.16 inclusive. Plot the maximum instrument response (eg peak height) against μg/l lead or cadmium. The calibration curve is norally linear to 100 μg/l for lead and to 10 μg/l for cadmium; 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, the calibration standard in step C9.10 is not appropriate, nor is the range given in Section C1.4. In such a case the calibration standard chosen for step C9.10 should be the highest concentration on the linear portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

C12 Change of Concentration Range of the Method

If the lead concentration in the sample is likely to exceed 100 μg/l, or the cadmium concentration is likely to exceed 10 μg/l, an appropriately smaller aliquot of the sample must be taken for analysis. To this volume of sample, V ml, add sufficient 50% V/V hydrochloric acid so that there is the same total volume of 50% V/V hydrochloric acid present as there would be in 200 ml of sample. Dilute with water to 200 ml and proceed as in step C9.1 onwards. It is necessary to alter the calculation of the result, step 9.17, as follows:

$$A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 100 \times \frac{200}{V} \text{ μg/l lead}$$

and

$$A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 10 \times \frac{200}{V} \text{ μg/l cadmium}$$

C13 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.

C13.1 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of lead or cadmium 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 glass apparatus used for the determination of these metals solely for this purpose and to carry out a preliminary series of blank determinations to ensure low blank values before analysing any samples.

C13.2 Lead and cadmium content of the water used for blank determinations

If the water used for the blank determinations contains either lead or cadmium the corresponding results will be falsely low. The importance of these errors depends on the lead and cadmium concentrations of the blank water and the concentrations of interest in the samples. Ideally the lead and cadmium content of the water and cadmium used for each blank determination should be measured and an appropriate correction made. An upper limit for the lead or cadmium content of the water can be calculated by converting the maximum instrument response (eg peak height) to concentration units. If the concentration obtained is negligible compared with the concentrations of interest in the samples no further action is required. If the concentration obtained is not negligible then the procedure which follows should be used to determine the lead and or cadmium content of the water:

(a) To each of two 500-ml borosilicate glass beakers add 200 ± 5 ml of water and 0.40 ± 0.05 ml of 50% V/V hydrochloric acid.

(b) To each of two 500-ml borosilicate glass beakers add 400 ± 10 ml of water and 0.40 ± 0.05 ml of 50% V/V hydrochloric acid.

(c) Cover all beakers with clean watch glasses and heat those from (b) on a hot plate until the volumes in them have been reduced to approximately 200 ml. Add a further 200 ± 5 ml of water to each beaker from (b) and continue heating until the volumes are reduced to 200 ± 5 ml. Cool the solution to room temperature.

(d) Analyse the contents of all four beakers as described in Section C9 and let the measured maximum instrument responses W_1^I and W_2^I for the two unheated beakers and W_1^{II} and W_2^{II} for the two heated beakers.

(e) The lead or cadmium content of the blank water is equivalent to a maximum instrument response of

$$W = \frac{(W_1^{II} + W_2^{II}) - (W_1^I + W_2^I)}{4}$$

(f) The concentration of lead A_w, in the blank water is then given by

$$A_w = \frac{W}{\bar{C} - \bar{B}} \times 100 \text{ µg/l lead}$$

The concentration of cadmium, A_w, in the blank water is given by

$$A_w = \frac{W}{\bar{C} - \bar{B}} \times 10 \text{ µg/l cadmium}$$

(See step C9.17).

C13.3 Interfering substances

See Section C3. The effect of possible interfering substances may be determined by analysing samples spiked with lead and/or cadmium and various concentrations of the potential interfering substance.

C13.4 Calibration standards

The calibration curve for this method has been found to be linear though its slope may vary from one set of determinations to another. Such variations are caused by changes in the sensitivity of the atomic absorption spectrophotometer. Therefore a calibration standard must be run for each batch of analyses and steps C9.10 onwards give the necessary procedure. This procedure assumes a linear calibration curve and the linearity must be checked (see Section C11).

C14 Checking the Accuracy of Analytical Results

(For further information see another publication in this series(5).)

Once the 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 a standard solution of lead and of cadmium of suitable concentration be analysed at the same time and in exactly the same way as normal samples (see Section C5.8.2 and step C9.10). The results obtained should then be plotted on quality control charts which will facilitate detection of inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated.

C15 Estimation of the Accuracy of Analytical Results using the Cadmium Method

C15.1 Introduction

Quantitative investigation of the accuracy achievable when the cadmium method is used appears to be limited to work at the Water Research Centre (Medmenham Laboratory). Before firmly recommending the method for general use, it is desirable to know the accuracy achievable in other laboratories. It would, therefore, be of great value if any laboratory using or considering the use of this method could estimate the accuracy of its own analytical results and report the finding to the Secretary of the Department of the Environment's Standing Committee of Analysts (for address, see the end of the booklet).

The precision achieved and the effects of any interfering substances that may be present in samples are of particular interest. Any information on these aspects would be useful, but the value of such information would be greatly enhanced if it were obtained to a common plan so that the information can be compared and valid conclusions drawn. Accordingly, suggestions for a suitable experimental design and analysis of results are given in the following sections and it is strongly urged that laboratories follow this design whenever possible. The design has been chosen to be as simple as possible; more complex designs are possible and would give more information.

C15.2 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 cadmium in the sample analysed and on the type of sample, eg worse precision may be obtained with samples than with standard solutions. For these reasons the basic design recommended is the analysis of one portion or each of the following solutions on each of n days, where n is at least 5 and preferably up to 10.

Solution No	Description
1	Blank
2	Another blank
3	Standard solution 1.0 μg/lCd
4	Standard solution 10.0 μg/lCd
5	Typical sample
6	Same sample spiked with 10.0 μg/lCd

It is essential that these solutions be treated exactly as if they were samples and the procedure specified in Section C9 of the method be rigidly followed. These solutions should be analysed in random order in each batch of analyses. Solutions 1 to 4 should be prepared each day exactly as described in the method and should contain the same amount of hydrochloric acid as is present in the samples. The same batch of water should be used on each day to prepare all four solutions. For solutions 5 and 6 a total of 5 litres of typical sample are required. Prepare solution 6 each day when required

by spiking solution 5 as follows: add with a bulb pipette 1.00 ml of an intermediate standard cadmium solution to 100 ml of solution 5. (The intermediate standard cadmium solution is prepared by diluting 10.0 ± 0.01 ml of standard cadmium solution A with water to 100 ml in a calibrated flask.) When analysing solution 6 it will be necessary to take into account Section C12 and to take an appropriately smaller aliquot. The total period of the tests may be any convenient time so long as the cadmium concentration in solution 5 does not change appreciably (up to 2 weeks). The results of the analyses of solutions 5 and 6 will provide a check on the effect of sample type on precision. Any deviation of the recovery of spiked cadmium from 100% may give an indication of the presence of interfering substances.

C15.3 Evaluation of Results

The raw experimental results may be sent direct to the Department of the Environment for evaluation together with the results obtained from the standards used to establish the calibration curve in each batch of analyses. However, for those laboratories wishing to make the calculations themselves, the details are given below.

C15.3.1 Convert all results to concentrations as described in the methods. Deduct the first of the two blank values (solution 1) from each of the other solution values.

C15.3.2 Calculate the mean concentration of the n results for each solution.

C15.3.3 Calculate the standard deviation, s, of the n results for each solution from:

$$s = \sqrt{\frac{\Sigma(x_1 - \bar{x})^2}{n-1}}$$

where x_i = the result from the ith batch
$\bar{x}$ = the mean value of X_i.

C15.3.4 Calculate the within-batch standard deviation, s_w, of the blank from:

$$s_w = \sqrt{\frac{\Sigma(x_{1i} - x_{2i})^2}{2n}}$$

where x_{1i} = 1st blank result (solution 1) from the ith batch
x_{2i} = the 2nd blank result (solution 2) from the ith batch.

C15.3.5 Calculate the mean percentage recovery, R, of the spiked cadmium in solution 6 from:

$$R = \frac{(\bar{x}_6 - \bar{x}_5)}{10} \times 100$$

where $\bar{x}_5$ = the mean value of the results for solution 5
$\bar{x}_6$ = the mean value of the results for solution 6.

C15.3.6 Summarize the results as in the following table:

Solution	No of results n	Mean cadmium Concentration µg/l	Standard Deviation µg/l	Mean Recovery
2 Blank				–
3 Standard, 1.0 µg/l Cd				–
4 Standard, 10.0 µg/l Cd				–
5 Sample				–
6 Solution 5 + 10.0 µg/l Cd				

The appropriate sample description should be entered in the space for solution 5. The standard deviation from step C15.3.4 is entered for the blank solution 2 and the standard deviations from step C15.3.3 are entered for solutions 3 to 6.

C15.4 A similar procedure may be used for lead if the accuracy of lead determinations is questioned.

C15.5 Results should be sent to the address given at the end of this booklet.

C16 References

(1) Water Research Associaton, Medmenham, *Technical Inquiry Report, TIR No 254*, August 1972.

(2) Water Research Centre, Medmenham, *Technical Report 28*, July 1976.

(3) Brown E, Skougstad M W and Fishman M J, *Techniques of Water Resources Investigations of the United States Geological Survey*. United States Government Printing Office, Washington 1970, 105.

(4) Department of the Environment, File WS/646/7, Paper SCA/MG/75/66, September 1975.

(5) *General Principles of Sampling and Accuracy of Results 1980*. HMSO, in this series.

D Lead in Potable and Clean Waters by Atomic Absorption Spectrophotometry (Dithiocarbamate — 1.1.2-trichloro, 1.1.2-trifluoroethane back extraction method). Tentative.

D0 Introduction

As mentioned in Section C3 for the accurate determination of traces of lead, it is advisable, often essential to separate the lead from the major cations prior to determination by Atomic Absorption Spectrophotometry. Method C uses an APDC/MIBK separation; but that method suffers from the following four problems:

(1) Toxicity and flammability of MIBK solvent.

(2) Instability of metal APDC complexes in MIBK.

(3) Emulsion formation with some raw and river derived waters.

(4) Problems of nebulizing organic solvents.

This slightly lengthier method was devised to overcome these difficulties.

Although not thoroughly tested, the method has also given satisfactory analyses for cadmium in two laboratories, using the 228.8 nm wavelength as in Method C.

Note: Throughout this method lead is expressed as the element Pb.

D1 Performance Characteristics of the Method

(For further information on the determination and definition of performance characteristics see another publication in this series(1).)

D1.1 Substance determined

All forms of lead likely to occur in potable waters.

D1.2 Type of sample

Potable, ground and clean river waters.

D1.3 Basis of method

Extraction of substituted dithiocarbamato-lead complexes into 1.1.2 – trichloro – 1.2.2 trifluoroethane, back extraction with dilute nitric acid followed by flame atomic absorption spectrophotometry.

D1.4

Range of application (a)

Up to 100 μg/l lead.

D1.5 Calibration curve (a)

Linear to at least 80 μg/l lead.

D1.6 Standard deviation (a)

Sample type	Mean conc found µg Pb/l	deviation %	Standard std. dev.	Relative
Standard solution (86.93 µg/l)	87.5	0.5	0.6	
Surface water sample	28.1	0.4	1.5	
Ground water sample	81.7	0.9	1.1	
Control standard (50.0 µg/l)	50.7	0.6	1.2	

D1.7 Limit of detection (a)*

1–2 µg/l.

D1.8 Bias

−c5% to +c1%.

D1.9 Interferences

Although two valent transition metals could interfere they are unlikely so to do. See section D3.

D1.10 Time required for analysis (a)

Operator and Total Analytical times the same, about 3–4 hours for 1–10 samples.

(a) These data were obtained at the Cambridge Regional Standards Laboratory, Anglian Water Authority.

*Only duplicate single blank and calibration standard samples were used when obtaining these data.

D2 Principle

The lead complexes formed by reaction with two dithiocarbamates is extracted into 1.1.2 – trichloro – 1.2.2 trifluoroethane, back extracted into dilute nitric acid and the amount of lead in this (second) aqueous extract is determined by flame atomic absorption spectrophotometry.

D3 Interferences

Two valent transition metal ions could interfere if present in relatively large amounts by competing for the extractant. Repetition of steps D5.5–D5.9 and D5.12 onwards using the discard from the original D5.8 step as sample would ascertain whether this was occurring.

D4 Hazards

The exhaust fumes from the atomic absorption spectrophotometry are toxic and must be ducted away. The solvent is volatile and may be narcotic, good ventilation is required. Dithiocarbamates are toxic.

D5 Reagents

Note, Analytical Reagent grade chemicals should be used in Section D5.4 onwards.

D5.1 Water

Good quality deionized or distilled water is suitable. Should the quality require checking take a 10 litre sample of the reagent water, add 1–2 ml of hydrochloric acid (d_{20} 1.18) and concentrate to 1 litre. Analyse as a sample, comparing the signal obtained with that from an unconcentrated sample of the same reagent water.

D5.2 Hydrochloric acid (d_{20} 1.18).

D5.3 1.1.2–trichloro–1.2.2 trifluoroethane — technical grade or better. Hereafter referred to as Solvent.

D5.3.1 Used Solvent may be recovered for reuse. Collect the lower layer from step D5.16. Wash thoroughly in a separating funnel with two successive equal volumes of tap water, dry over anhydrous (ignited at 500°C) sodium sulphate and redistill, collect the fraction boiling between 45–48°C.

D5.4 Buffer Solution

25.00 ± 0.05 ml of acetic acid and 120.0 ± 0.1 ml water are placed in a 250 ml beaker. A 1:1 mixture of water and d_{20} 0.880 Ammonia solution is added with constant stirring and monitoring of the pH with a glass electrode until the pH is 4.5 ± 0.1. (This requires approximately 20 ml of 50% ammonia). The volume is made up to 200 ml. The buffer should be stored in a polythene bottle.

D5.5 Extraction Reagent

0.50 g ± 0.05 of ammonium pyrrolidine dithiocarbamate (APDC) and 0.50 g ± 0.05 of diethylammonium diethyldithiocarbamate (DDDC) is dissolved in 50.0 ml ± 0.1 ml of water in a 125 ml polyethylene bottle. 50 ± 1 ml of Solvent (D5.3) is added and the bottle shaken for approximately 60 seconds. The reagent is stored over the Solvent, and is stable for 24 hours. Keep in the dark.

D5.6 Methyl Orange Solution

Dissolve 0.10 g ± 0.01 methyl orange (sodium salt) in 100 ± 1 ml of water, adding a few drops of dilute ammonia solution to ensure complete dissolution.

D5.6.1 Colour blind technicians and some others have difficulty seeing the end point in step D8.3. In this instance a pH meter reading of 3.8–3.9 may be used instead.

D5.7 10% V/V Ammonia Solution

Add 10 ± 0.2 ml of d_{20} 0.880 ammonia solution to 90 ± 2 ml water. Store in a polythene bottle.

D5.8 Nitric Acid

D5.9 A calibration blank is prepared from water, which must have a lead content that is negligible compared to the minimum concentration of interest (See D5.1), to which is added the same amount of hydrochloric acid per litre as used in the preservation of samples (see Section D7).

D5.10 A calibration standard is prepared as the calibration blank except that a standard solution of lead is added to give a final concentration of 80 µg Pb/l. 40.00 ± 0.05 ml of solution C5.8.2 made up to 1 litre with water in a calibrated flask.

D5.11 A control standard is prepared as the calibration blank, but from a different stock solution of lead, and is made to contain 50 µg Pb/litre. 25.00 ± 0.05 ml of solution C5.8.2 is made up to 1 litre with water in a calibrated flask.

D5.12 Dilute (1:10) Nitric acid — for cleaning purposes. Take 1 volume of nitric acid (d_{20} 1.42) and pour into 9 equal volumes of water. Stir to mix. (Accuracy of measurement required: ± 5%).

D6 Apparatus

D6.0 Cleanliness

Apparatus should be cleaned by soaking overnight in 10% nitric acid, followed by rinsing with water.
Separating funnels may be cleaned immediately before use by carrying out a 'blank' extraction and discarding both phases.
Disposable tips for the micropipettes may be used without special cleaning.
Routine cleaning of the stoppered test tubes is accomplished by rinsing with water, rinsing with 10% nitric acid, rinsing with water again followed by rinsing with acetone. Finally, the tubes are dried with a stream of oil free, dust free air.

D6.1 250 ml glass conical shaped separating funnels with PTFE stopcocks and glass stoppers.

D6.2 50 ml test tubes with polyethylene stoppers.

D6.3 Air interface micropipettes 1000 µl and 100 µl.

D6.4 An atomic absorption spectrophotometer equipped for an air/acetylene flame and with a lead hollow cathode lamp. Scale expansion should be used to ensure that adequate recorder response is achieved with the highest calibration standard used. Background correction is not essential.

D7 Sample Collection and Preservation

Samples should be collected in 1 litre polyethylene bottles and acidified to pH 2.5 ± 0.3 with hydrochloric acid D5.2 to act as a preservative.

D8 Analtyical Procedure

Step	Procedure	Notes
	Extraction Procedure	
D8.1	Transfer 20 ml ± 2 ml or Solvent to a 250 ml separating funnel.	
D8.2	Add 200 ml ± 2 ml of sample to the separating funnel.	
D8.3	Add 3 drops of methyl orange solution and adjust the pH by addition of 10% ammonia solution dropwise to a peach coloured end point (notes a and b).	(a) The ammonia is best added from a pasteur pipette. (b) The sample should be kept well swirled during pH adjustment. See D5.6.1 if this end point causes problems of detection.
D8.4	Add 1.0 ml ± 0.02 ml of acetate buffer solution (D5.4) (note c) and swirl to mix.	(c) Use an air interface micropipette.

Step	Procedure	Notes
D8.5	Add 1.0 ml ± 0.02 ml of extraction reagent (D5.5) (note e), stopper and immediately shake the funnel vigorously for 120 ± 5 seconds (notes d and e).	(d) This must be done immediately to prevent precipitation of complexes that may be slow to extract. (e) Do not release pressure through the tap, it must remain free of aqueous phase. Pressure buildup should be released (carefully) through the stoppered top after shaking for about 5 seconds.
D8.6	Allow the phases to separate, remove the stopper from separating funnel, and run the lower, solvent layer into a dry (stoppered) test tube (note f).	(f) Care should be taken not to allow aqueous phase to enter the tap.
D8.7	Add a further 10 ml ± 1 ml of Solvent to the separating funnel and shake for 30 ± 3 seconds (note e).	
D8.8	Allow phases to separate and drain off the lower phase into the same test tube used in D8.6. Discard the aqueous phase (note g).	(g) See Section D3 if interference has been suspected.
D8.9	Repeat stages D8.1 to D8.9 using 200 ml of acidified lead free water (note h).	(h) Duplicate blanks and standards are preferred.
D8.10	Repeat stages D8.1 to D8.9 using 200 ml of 80 µg Pb/l standard solution in place of the sample (note h).	
D8.11	Repeat steps D8.1 to D8.9 using a 50 µg Pb/l standard solution in place of the sample.	
	Back Extraction	
D8.12	Add 0.2 ml ± 0.02 ml conc nitric acid to the Solvent phase in the stoppered test tubes and mix (note i).	(i) Use an air interface micropipette for the acid addition.
D8.13	Wait for **at least** five minutes and 10.00 ± 0.04 ml water and swirl to mix (note j).	(j) Use a bulb pipette for the add water addition.
D8.14	Wait for **at least** 30 minutes.	
D8.15	Shake vigorously for 20 seconds ± 2 seconds.	
D8.16	Allow the phases to separate (note k).	(k) The samples may be left overnight at this state, if desired.
D8.17	Remove and keep the upper aqueous layer.	
	Measurement of Extracts by AAS	
D8.18	Set up the AAS instrument according to the manufacturer's instructions for lead analysis at 217 nm, set the instrument zero with water.	

Step	Procedure	Notes
D8.19	Aspirate water, in the manufacturer's prescribed optimum manner and record the reading (A_{B1}). (Note 1).	(1) In the calculation section these absorbances are indicated by A_{SX} for samples where x is the sample number and similarly A_{BX} for blanks, A_{CX} for the calibration standards and A_{QX} for control standards, where x is 1 or 2.
D8.20	In like manner, aspirate the extracts from the samples, blanks and standards in the following order, recording each reading. Each extract is analysed twice. The order of aspiration of extracts should be standard 1, standard 2, blank 1, blank 2. Samples in order 1 to n (including at a random position one control standard). Samples in reverse order n to 1 (with one control standard included at a random position), blank 2, blank 1, standard 2, standard 1 (note 1).	
	Calculation of Results	
D8.21	Correct each extract absorbance for the mean of its nearest pair of water blank absorbances. The corrected absorbance for sample j is S_j where $S_j = A_{Sj} - \frac{A_{B^1} + A_{B^2}}{2}$	
D8.22	Calculate the mean blank absorbance (S_B) from the corrected absorbances of the two aspirations of each blank extract.	
8.23	Calculate the mean absorbance for the 80 μg Pb/l standard (S_S) from the corrected absorbances of the two aspirations or each of the 80 μg Pb/l standard extracts.	
D8.24	Calculate the mean absorbance (S_{Cj}) from the corrected absorbances of the two aspirations of sample j. Do this for all samples.	
D8.25	Calculate the concentration of lead in sample j from the following formula: $C_j = 80 \times \frac{(S_{Cj} - S_B)}{(S_S - S_B)}$ where C_j is the lead concentration in μg Pb/l in sample j, S_{Cj} is the mean corrected absorbance reading found on the extract of this sample (see step D8.24), S_B is the mean corrected absorbance of the blank (see step D8.22) and S_S is the mean corrected absorbance given by the extract of the 80 μg Pb/l standard solution (see step D8.23).	

D9 Analytical Quality Control

D9.1 Carry out the above calculations to determine the mean lead concentration in the 50 μg/l control standards. Any discrepancy must fall within the accepted limits of error. If the discrepancy is unacceptable, investigate cleanliness, technique, reagent purity and so on.

D9.2 Plot the mean control standard on a quality control chart (2, 3). Investigate any trends or seriously erratic results.

D9.3 Linearity should be checked when a new batch of reagents is started, or if instrumental or extraction problems are suspected, by analysing a series of standards of 0, 20, 40, 60, 80, 100 μg Pb/1.

D10 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.

D10.1 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of lead or its 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 glass apparatus used for the lead determinations solely for this purpose and to carry out a preliminary series of blank determinations to ensure low blank values before analysing any samples.

D10.2 Lead content of the water used for blank determinations

If the water used for the blank determinations contains lead the results will be falsely low. The importance of this error depends on the lead concentration of the blank water and the concentrations of interest in the samples. Ideally the lead content of the water used for each blank determination should be measured and an appropriate correction made. An upper limit for the lead content of the water can be calculated by converting the maximum instrument response (eg peak height) to concentration units. If the concentration obtained is negligible compared with the concentrations of interest in the samples no further action is required. If the concentration obtained is not negligible then the procedure which follows should be used to determine the lead content of the water:

(a) To each of two 500-ml borosilicate glass beakers add 200 ± 5 ml of water and 0.40 ± 0.05 ml of 50% V/V hydrochloric acid.

(b) To each of two 500-ml borosilicate glass beakers add 400 ± 10 ml of water and 0.40 ± 0.05 ml of 50% V/V hydrochloric acid.

(c) Cover all beakers with clean watch glasses and heat those from (b) on a hot plate until the volumes in them have been reduced to approximately 200 ml. Add a further 200 ± 5 ml of water to each beaker from (b) and continue heating until the volumes are reduced to 200 ± 5 ml. Cool the solution to room temperature.

(d) Analyse the contents of all four beakers as described in Section D8 and let the measured maximum instrument responses W_1^1 and W_2^1 for the two unheated beakers and W_1^{11} and W_2^{11} for the two heated beakers.

(e) The lead content of the blank water is equivalent to a maximum instrument response of

$$W = \frac{(W_1^{11} + W_2^{11}) - (W_1^1 + W_2^1)}{2}$$

(f) The concentration of lead A_w, in the blank water is then given by

$$A_w = \frac{W}{S_S - S_B} \times 80 \text{ μg/l lead (for } S_S \text{ see D8.23 and for } S_B \text{ see D8.22)}$$

D10.3 Interfering substances

See Section D3. The effect of possible interfering substances may be determined by analysing samples spiked with lead and various concentrations of the potential interfering substance, and also by investigating whether the extraction into solvent is satisfactory. If it is not, it may be necessary to add extra solvent extraction steps or increase the amounts of extractants D5.3 and D5.5 used.

D10.4 Calibration standards

The calibration curve for this method has been found to be linear, though its slope may vary from one set of determinations to another. Such variations are caused by changes in the sensitivity of the atomic absorption spectrophotometer. Therefore a control standard must be run for each batch of analyses and step D9.3 gives the necessary procedure. This procedure assumes a linear calibration curve and the linearity must be checked (see Section D9.3).

D11 Change of Concentration Range of Method

If the lead concentration in the sample is likely to exceed 100 μg/l an appropriately smaller aliquot of the sample must be taken for analysis. To this volume of sample, V ml, add sufficient hydrochloric acid D5.2 so that there is the same total volume of hydrochloric acid present as there would be in 200 ml of sample. Dilute with water to 200 ml and proceed as in Section D8. It is necessary to alter the calculation of the result, step D8.25 by multiplying the found concentration by the dilution factor $\frac{200}{V}$.

D12 References

(1) *General Principle of Sampling and Accuracy of Results 1980.* HMSO in this series.

(2) British Standards *BS 5700 to 5703* inclusive.

(3) Davey D J and Hunt D T E, The use of cumulative Sum Charts in Analytical Quality Control. *WRC Technical Report TR174.* Water Research Centre, Medmenham 1982.

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

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