Methods for the Determination of the Metals Aluminium, Cadmium, Chromium, Cobalt, Copper, Iron, Lead, Manganese, Nickel, Uranium, Vanadium and Zinc in Marine, Estuarine and Other Waters by Stripping Voltammetry or Concentration and Atomic Absorption Spectrophotometry 1987

(with notes on other metals and related techniques)

Methods for the Examination of Waters of Associated Materials

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In several places in this booklet mention is made of specific makes of equipment or products used in obtaining the test data. This is no way endorses these particular items. Any similar equipment or product giving the same or better results may be substituted.

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Test data for Methods

A—H University of Liverpool
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I WRC Medmenham Laboratory (in part under DOE Research Contracts) with additional information from North West WA and South West WA

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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 These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print.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; this 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 nine 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
2.0 Microbiological methods
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological monitoring
8.0 Sewage Works Control 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 1987

Warning to Users

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

Local Safety Regulations must be observed.

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

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

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

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

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. The methods in this booklet involve the use of compressed gases. Cylinders should be securely fastened and fitted with pressure regulators and valves in working order. No apparatus should be allowed to come to a pressure sufficient to burst it. Glass apparatus should be protected by a lute in the supply line. A lute is a teepiece dipping into oil or water to a sufficient depth that the gas will normally pass through the apparatus and not bubble out of the lute, but if the apparatus blocks, the lute tube is sufficiently wide bored to take the full gas flow. Note that most gases cool on expansion and if wet can cause ice blockage. Hydrogen is an exception, and can heat on expansion and even ignite in air at the leak. 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 require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical 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 specialised hospital.

Safety while Sampling

For detailed recommendations affecting safety while sampling see the Safety section in Ref 57.

Introduction

1 General Points

1.1 Marine, estuarine and similar waters, because they contain large amounts of dissolved solids, are not suitable for the direct determination of trace metals by Atomic Absorption Spectrophotometry. However, they may be suited to direct electrochemical methods if these are sensitive enough. Alternatively, the trace element may be separated, and concentrated by solvent extraction or coprecipitation.

This booklet contains a selection of such methods developed at the Department of Oceanography, University of Liverpool, the Water Research Central Medmenham, and North West Water Authority, for the analysis of sea water. During the course of this work it was found that some of these methods are also directly applicable to potable and other fresh waters, some with very low limits of detection. Where this is known, it is indicated in the method title.

Electrode Stripping Voltammetry is a very sensitive method for many metals (Ref 16), but until recently has not been widely considered in the water industry due to the problem of obtaining reproducible electrodes. This has now been overcome by at least two instrument manufacturers. Short training courses in this technique are now available.

Both the Voltammetric and Solvent Extraction AAS methods determine dissolved metals and require careful prior filtration. 'Particulate metals' (or suspended metals as they are sometimes called) can also be determined after solution or, if sufficient solid is available, direct X-ray fluorescence analysis of the solid on the filter may be used (34). The following table shows the methods which are suitable for the various determinations.

Methods A—H are Voltammetric
Methods I and J are Solvent Extraction AAS which, whilst satisfactory for ascertaining compliance with directives and similar standards, are not sensitive enough for unmineralised open waters not close to land.

Method K is a Precipitate Collection AAS method
Method L applies only to particulate matter

1.2 The methods recommended are suitable for the determination of 'dissolved metals' and 'particulate metals'. 'Dissolved metals' are defined as those in the filtrate after passing the sample through a 0.45 μm filter and 'particulate metals' are defined as those in the material retained by the filter.

1.3 The basic methods consist of filtration followed by:—

(a) for 'particulate metals', acid digestion of the material retained by the filter and determination of the metal concerned by flame atomic absorption spectrophotometry;

(b) for 'dissolved metals', oxidative pretreatment using persulphate, ozone or photochemical oxidation by oxygen and ultraviolet irradiation) on the filtrate, followed by either direct electrode stripping voltammetry or a concentration step using complexation with mixed carbamate/solvent extraction and followed by determination of the metal concerned by flameless atomic absorption spectrophotometry (flame atomic adsorption spectrophotometry may be used in some circumstances).

2 Sampling

2.1 General

The application of recent technological developments to instrumental analytical techniques has made it possible routinely to carry out analysis for many heavy metals occurring in natural waters at the submicrogram per litre level. As a consequence of this, it has become increasingly apparent that the sampling, storage and filtration of such samples must be undertaken with great care and an understanding of the changes that are likely to occur at these stages. The most obvious change is that of contamination of the sample, and analysts should be aware that it is particularly difficult to avoid contamination by lead and zinc. Less obvious is the fact that loss of metals can occur by adsorption onto the walls of the samplers, storage containers and filtration apparatus. Storage of unfiltered samples can result in exchanges between the particulate and dissolved forms. There is also the possibility that transformations of chemical species can occur during storage. Finally, there is the possibility of the presence of the determinand metals in the reagents used. Precautions must be taken to minimize all these effects in order to achieve satisfactory results at submicrogram per litre levels. Some of these aspects are discussed in more detail in the Sections below.

The general principles of sampling have been adequately reviewed elsewhere[1,2].

There are two basic requirements for the successful sampling of water masses for trace metals. First, the sample must be representative of the water mass and second, it must be collected and maintained in an unaltered state until the analysis can be carried out. The collection of representative water samples in estuarine and coastal waters requires consideration both of the three spatial dimensions as well as time. Time related sampling is particularly important in such waters due to the influence of tidal currents. Indiscriminate collection of water samples from a medium that is varying widely both in space and time is likely to produce confusing data of little practical value.

2.2 Contamination

Contamination of samples during collection is probably the most significant factor contributing to the wide variability and anomalous results reported in the literature for many trace metals. There has been a steady decrease in the reported concentrations of many trace metals in marine waters as more refined sampling techniques employing greater control of contamination have been introduced. However, although the basic problems have been recognised for a quarter of a century[3] sampling is probably still the weakest link in marine trace metal studies. Guidance on appropriate sampling techniques is divided into three parts dealing with surface, subsurface sampling and subsequent handling.

2.3 Surface Sampling

Surface samples are usually collected by hand either from the Research Vessel, or preferably from a small boat positioned some distance away. There are three potential sources of contamination:—

(a) The Research Vessel/Boat. The Research Vessel is a major source of contamination derived from antifouling materials, paint and rust flakes, exhaust particulates, refuse, waste oils etc. It is preferable to use a small boat, such as an inflatable, as a sampling platform, positioning the craft to windward of the Research Vessel and far enough away to be outside the range of the contaminant material. However, if this is not practicable, samples should be taken from the bow of the Research Vessel as it approaches the sampling point.

(b) The Sampling Equipment. All equipment used for surface sampling should be made of plastic materials, scrupulously cleaned prior to use and maintained in a clean condition. This latter criterion can be difficult to achieve when operating in the confined and inevitably dirty environment found on most small boats. However, it is usually practicable to keep the equipment and both full and empty sample containers in sealed polyethylene bags, only opening this protective coat for the few minutes when they are in use. It is advisable to pre-test plastic

bottles to ensure that they neither release metals into solution, nor adsorb them from solution. This may be ascertained by storage tests with known samples. See also Section 4.

(c) The Surface Microlayer. The sea surface microlayer is itself a specialized region of the marine environment which is known to be significantly enriched with trace metals[4]. If possible, surface water samples should be obtained in such a manner that this layer is excluded, unless this layer itself is being investigated.

The preferred sampling procedure for surface waters is that proposed by the participants in the Lead in Seawater Workshop[5]. Sampling is undertaken from a small inflatable craft positioned to windward of the Research Vessel. Samples are collected from the bow, with the boat moving slowly forward into the surface current. Sealed sample bottles are forced beneath the surface microlayer, their caps removed and the bottles allowed to fill while ensuring that none of the surface layer is entrained with the sample. When the bottle is completely full it is recapped before being removed from the water. The sample bottles are stored in plastic bags both before and after filling. If this procedure cannot be used, adequate samples may be obtained using a plastic bucket and line from the bow of a ship steaming gently into the wind; however, in this case collection of the surface microlayer and associated debris will be inevitable. See also Ref 58.

2.4 Sub-surface Sampling

Some of the problems associated with the collection of surface samples such as contamination from the sampling equipment are also important in sub-surface sampling. However, the problems associated with the contamination from the surface microlayer and its associated debris can usually be eliminated. Sub-surface water samples are collected either by pumping or by trapping discrete columns of water at depth using a sampling bottle. The suspension line used for the equipment and its drum may cause problems, and it is preferable to use either plastic such as Kevlar or unlubricated stainless steel wires and to cover the drum with polyethylene sheet. The systems described below can also be used for the collection of water samples close to the surface.

(a) By Pumping. (Suitable only down to 1000 m). The collection of water samples by pumping has many attractive features[6,7]. Very large volumes of water can be obtained relatively quickly and both vertical and horizontal profiles can be obtained easily. However, all pumping systems have a degree of uncertainty associated with their flushing efficiency, which can lead to cross contamination of samples. Peristaltic pumps often submersible utilising PTFE or high purity polyethylene tubing should be used, since in line impeller pumps inevitably produce contamination even when constructed of plastic coated components[8].

(b) By Sampling Bottle. Water bottles are the most commonly used method of collecting sub-surface water samples. The majority of modern water bottles are made of plastic, but the use of neoprene seals and coated metallic components can be a source of trace metal contamination. A wide variety of sizes and types is available[2,6] and the suitability of these samplers for trace metal studies has been reviewed by a number of authors[6,7,8]. In order to eliminate problems caused by contamination in the surface microlayer, sub-surface sampling bottles should pass through the surface layer in the closed position. There are two types of commercially available samplers which fulfil this requirement. The simplest consists of a weighted polypropylene bottle with a removable polypropylene plug stopper. The sampler is lowered, in the closed position, to the required depth and the plug stopper withdrawn by pulling on a nylon connecting line. This system has the disadvantage that only one sample can be collected at a time and the system is only effective to depths of *ca.* 10–20 m. The alternative system uses double acting water bottles, of the Go-flo type that are opened at depth (usually 10 m) and then closed (sequentially) electrically or by a messenger weight sliding along the support cable. In conclusion, all sampling equipment used for the collection of water samples for trace metal analysis in marine, estuarine and coastal waters should be made of plastic and maintained in a scrupulously clean condition. The procedure used for the collection of the sample should be designed so as to avoid contamination of the sample with the surface microlayer.

2.5 Subsequent Handling

Much contamination can occur if the sample must be transferred from a special sampler to a sample bottle. Analyses for very low levels of determinand are very prone to error due to pick up from the atmosphere during such transfers, which are best made in cabins or cabinets supplied with purified air. If samples are taken directly into the final sample bottle, care should be taken that the stoppers are tight but do not stick, and that all sample on the outside of the bottle is removed by washing and or blotting, so that none subsequently evaporates, so causing contamination when the bottle is opened.

3 Filtration

3.1 Natural waters contain suspended particulate material in amounts varying from a few μg/l to tens of mg/l. If the particulate material content is less than 1 mg/l its analysis for trace metal content may be considered unimportant. For trace heavy metal measurements it is desirable to separate the sample into dissolved and particulate fractions by filtration. The subject of filtration has been reviewed by Riley[6]. It has become the practice to regard a filter of average pore size of 0.45 μm as the barrier between the dissolved and particulate fractions. It must be noted that the use of the 0.45 μm filter is purely arbitrary and it has no special significance and also that the retentivity of the filter will vary with particle size, the volume filtered and the amount of particulate matter present.

3.2 The filtration stage provides an opportunity for changes in the metal concentrations to occur. Contamination and/or loss by adsorption can occur if the wrong materials are chosen for the construction of the filter rig and the filter medium itself. The use of any metal in contact with the sample must of course be avoided. Whilst this is an obvious comment, what is less obvious is that metal should be avoided, or at least be plastic coated, in the construction of any part of the filtration rig. Experience has shown that eventually sea water will contact the metal parts, with the consequent high risk of corrosion products getting into the sample.

3.3 The choice of filtration rig depends to some extent on the volume of water that is required for analysis. In areas of very high metal and suspended load as little as 50 ml may be sufficient. For this a very simple device consisting of a 50 ml hypodermic syringe fitted with a Millipore Swinnex filter holder has been used. For open ocean work very specialized rigs have been built capable of filtering up to six litres very quickly. Unfortunately there is no commercially available rig which meets all the desirable requirements. So analysts are left with the necessity of building their own rig. Other factors to be considered are portability and simplicity, since the rig may have to be used in the 'field'. Unless one is only concerned with the 'total' metals present, the sample must be filtered very shortly after collection to avoid possible changes in the dissolved: particulate ratio.

3.4 The choice of filtering medium is very important and the desirable properties of such have been described by Riley[6]. The most commonly used types are made of cellulose acetate—nitrate mixtures or of polycarbonate. Conventional cellulose papers should be avoided, as should glass fibre, with the exceptional case of mercury in the latter instance. The materials of construction of the filtration rig and the working area should be selected after taking note of the comments in the Introduction Sections 2 and 4 dealing with sampling and storage of saline water samples. Each step in the procedure must be performed with care to ensure that no changes occur in the concentrations of metals in the sample and the analyst must ensure by careful trial that the filtration step is performing satisfactorily.

3.5 The procedure described in the Method I Section I 11.5 is based on the experience of the University of Liverpool and Ministry of Agriculture, Fisheries and Food and has been successfully applied to samples from riverine, estuarine, coastal and pelagic environments. It should be noted that where it is necessary to obtain data on the weight of suspended load per unit volume of sample it may be desirable to take a separate sample for this, since the handling during weighing is a possible source of contamination. Membrane filters do become electrically charged on handling and difficulties can be experienced during weighting. To overcome this an antistatic radioisotope disc such as those supplied by Amersham International should be used.

4 Sample Storage

4.1 The storage container must be clean, otherwise contamination of the sample could occur. Loss of metals can occur by adsorption on to the walls of samplers, filtration apparatus and storage containers. Storage of unfiltered samples can result in exchanges between the particulate and the dissolved forms. There is also the possibility that transformations of chemical species can occur during storage. Procedures for sampling and storage of natural water samples have been adequately reviewed by Batley and Gardner.[9].

4.2 A wide range of materials have been examined as possible suitable contenders for use as storage containers. These vary from borosilicate glass through polyethylene to more exotic plastics like polymethyl pentane and fluorinated polymers (Batley and Gardner[9], Moody and Linstrom[10], Subramanian *et al.*[11]). It is now generally accepted that the most suitable materials are either high density polyethylene or Teflon. Subramanian *et al.*[11] report that Teflon is the only suitable material when zinc analysis is required. Use of plastic storage bottles does not preclude loss of metals from solution by adsorption or plating as films; such metals can often be recovered by an acid rinse after emptying; but bottles must have also been similarly treated prior to use, as some plastics contain traces of metal.

4.3 Various cleaning methods have been examined by Laxen and Harrison[12]. These range from use of the sample only, or of a detergent, to a series of acid washes with differing concentrations and sequences of hydrochloric, nitric and perchloric acids. The results of these investigations indicate that polyethylene containers soaked in 10% v/v nitric acid for 48 hours, followed by a deionized and distilled water rinse and drain drying, are suitable for storage of freshwater samples prior to analysis for zinc, cadmium, lead and copper. There is no reason to suppose that this is not also true for saline waters.

4.4 To prevent losses on storage due to adsorption, methods such as acidification, addition of complexing reagents, storing at low temperature and freezing have been tried. The most attractive method is undoubtedly that of freezing solid, since this does not require the addition of any reagents. However, this is not always practical since it has to be done immediately to be of use. The recommended method is that of acidification to a pH value of less than 2.5 with high purity nitric acid[9,11] the acidified sample being stored in a clean high density polyethylene container. If the sample is liable to fungal growth, a pH value of less than 1.5 may be required. Hydrochloric acid can be used instead of nitric acid.

5 Particulate Material

5.1 When analysing particulate material from saline water samples for trace metals a decision has to be made as to whether a complete dissolution of the sample, or merely an acid extraction should be performed. Whilst complete dissolution methods give an absolute answer they are often long-winded and impractical when large numbers of samples have to be analysed. It can be argued that in pollution studies one is primarily interested in metals of anthropogenic origin and not the lattice held lithogenic fraction. The non-lattice held fraction includes much material which is not anthropogenic and no technique will distinguish the anthropogenic material specifically. An acid extraction will separate a fraction of the metal which is more available and this will include the anthropogenic material. A complete dissolution may not give the required answer. Many reagents have been used to extract various fractions[13], but opinions differ as to what the results from any particular extraction mean. The fact that a particular method gives very reproducible results means just that, and not necessarily that all the metal has been extracted[14,15]. However, for reasons of practicability, the fact that metals of recent anthropogenic origin are probably more labile than those of lithogenic origin and that one is looking for trends and relative levels rather than absolute ones, the common practice is to perform an acid extraction. Users should ascertain which extraction best suits their purpose and state which they used in their report. See also Ref 38.

5.2 The use of hydrochloric acid alone is not sufficient since some organic debris will be present and may retard the extraction of some metals. The use of an oxidizing agent such as nitric acid alone does not give such an efficient extraction as a mixture of hydrochloric and nitric acids. This is thought to be due primarily to the hydrochloric acid complexing the iron present. At the Ministry of Agriculture Fisheries and Food laboratory it was found that a 3:1 hydrochloric/nitric acid mixture gave the most reproducible results and ones which it was felt could be best related to anthropogenic sources. When comparing results of analysis of particulate matter from different areas where the basic sediment type may differ, one should be careful that the extraction efficiencies are known or at least similar. Ideally, the total to acid extractable ratio should be determined at the beginning of a survey. Although the mixed acid extraction procedure could be carried out in glassware instead of the platinum-ware necessary for high temperature fusions or hydrofluoric acid extractions, leaching of metal traces from the glassware is a severe liability and PTFE is preferred for such extractions. PTFE also allows the use of hydrofluoric acid (21).

5.3 Note that the methods as given in this booklet include the pretreatments (acidification, filtration and oxidation) used to determine the test data.

6 Choice of Method

6.1 For completeness, metals not covered by this booklet are also listed, with the appropriate method reference.

6.1.1

Dissolved Metal	Method in this booklet	Other Method
Aluminium	G	
Antimony		31,42,73
Arsenic		32
Bismuth		42,16
Cadmium	A, I, K	65,71
Chromium	K	67
Cobalt	E, I	68
Copper	B, I. J	71
Gallium		76
Germanium		78
Indium		16 and ref therein, 77
Iron	H, I	
Lead	A, I. J	65,71
Manganese	I	
Mercury		29,30
Molybdenum		74,70
Nickel	E, I. J	68
Selenium		69
Silver		33,66
Thallium		16 and ref therein
Tin		75
Uranium	F	
Vanadium	C	22
Zinc	D, I	

6.1.2 Other method references 16 and 71–78 are to Stripping Voltrammetric methods, references 68–70 are to related Chronopotentiometric methods.

A booklet on multielement ICPS methods is in preparation. See also 58.

6.1.3 Particulate Metals

Solution of Sample: Ref 18, 21, also L

Analysis of Dissolved Sample: as for Dissolved Metal above and see also the following references:

Metal	Method or Reference
Aluminium	17, 58
Cadmium	19, 18, 34, 58
Chromium	L, 20, 18, 22, 34, 58
Cobalt	23, 22, 34, 58
Copper	24, 18, 22, 34, 58
Iron	25, 34, 58
Lead	19, 18, 34, 58
Manganese	26, 34, 58
Nickel	27, 18, 22, 34, 58
Uranium	34, 58
Vanadium	22, 34, 58
Zinc	28, 18, 22, 34, 58

Note the methods in Refs 34 and 58 can be adapted for the analysis of solid samples without prior solution. These and Ref 22 include many more metals not listed above.

6.1.4 Section I 11.4 gives a procedure for 'Total' metals (38) in which the particulate matter is leached prior to filtration.

6.2 Variation of the Procedure

If the analyst modifies a method, this variation should be mentioned in the report. Analysts must investigate the effect of such variation prior to commencing routine analyses.

6.2.1 Pretreatments

Acidification, filtration, oxidation and solution of particular matter are discussed elsewhere, especially earlier in this Introduction and in the notes at the end of Method I.

6.2.2 Substitutes for Ammonia

Ammonia is used in several of the methods given in this booklet. However, this can cause problems especially in large open plan laboratories where trace levels of ammonia are being determined nearby. Several alternatives are possible such as ethanolamine, and sodium or potassium bicarbonates. While it is known that these variants are practicable for some determinations, full evaluations have not been made. Users should first determine the required amount of their chosen alternative reagent to give the same effect as ammonia, and then check the effect on the analytical performance.

6.3 Combination of Stripping voltammetric Determinations

Two of the methods given, A and E, determine two metals. Other combinations are also possible. For a simultaneous determination of Cadmium, Lead and Copper using Oxine as complexant see Ref 71. Molybdenum cannot be included as the pH required is too different. In addition to the determination of copper and vanadium using catechol, iron and antimony may also be determined under similar conditions.

6.4 Glassy Carbon Electrodes

Commercial instruments with Glassy Carbon Electrodes unstead of a hanging mercury drop are also available. These can be used to determine mercury and gold, but not to as low a concentration as many other metals can be determined by either type of electrode.

7 Chrono-potentiometry

Chronopotentiometry is a very similar technique to stripping voltammetry which is less sensitive to interference from dissolved oxygen. Sometimes it is slightly less sensitive, but for some metals it is more sensitive. See references 68, 69 and 70 for applications to the analysis of Nickel, Cobalt, Uranium, Selenium and Molybdenum.

A

Direct Simultaneous Determination of Dissolved Cadmium and Lead in Fresh and Sea Waters by Differential Pulse Anodic Stripping Voltammetry using the Hanging Mercury Drop Electrode.

A1 Performance Characteristics of the Method

(For an alternative anodic stripping voltammetric method see Ref 71)

A1.1 Substances determined

Dissolved Cadmium (Cd) and Lead (Pb).

A1.2 Type of sample

Natural and sea waters which have been filtered (see section A8.1) and subjected to UV irradiation (see section A8.1).

A1.3 Basis of method

Cd and Pb are electro-deposited on a hanging mercury drop electrode and subsequently determined by differential pulse anodic stripping voltammetry (DPASV). (41,42).

A1.4 Range of application (a), (d).

Up to at least 4.5×10^{-7}M Cd (50.6 $\mu g\ 1^{-1}$) and 2.4×10^{-7}M Pb (49.7 $\mu g\ 1^{-1}$).

A1.5 Calibration curve (a), (d).

Linear to at least 4.5×10^{-7} M Cd (50.6 $\mu g\ 1^{-1}$) and 2.4×10^{-7} M Pb (49.7 $\mu g\ 1^{-1}$).

A1.6 Within Batch Standard Deviation (with 8 degrees of freedom)(d).

For additional test data see Ref 65

	Cd concentration nM	(ngl^{-1})	Standard Deviation nM	(ngl^{-1})
(b)	0.56	(63)	0.036	(4.0)
(b)	17.9	(2×10^3)	0.12	(13.5)
(c)	0.78	(87)	0.030	(3.4)
(c)	22.1	(2.5×10^3)	0.18	(20.2)

	Pb concentration nM	(ngl^{-1})	Standard Deviation nM	(ngl^{-1})
(b)	1.36	(282)	0.048	(9.9)
(b)	25.8	(5.3×10^3)	0.32	(66)
(c)	1.36	(282)	0.082	(17)
(c)	24.5	(5.1×10^3)	0.19	(39)

A1.7 Detection limit, (d)

(b) Cd : 1.1×10^{-10}M (12.4 ng 1^{-1})
Pb : 1.4×10^{-10}M (29.0 ng 1^{-1})

(c) Cd : 0.92×10^{-10}M (10.3 ng 1^{-1})
Pb : 2.4×10^{-10}M (49.7 ng 1^{-1})

A1.8 Sensitivity

(b) Cd : 0.56nM (63 ng 1^{-1}) gives a peak height of 2.3nA;
Pb : 1.36nM (282 ng 1^{-1}) gives a peak height of 5.8nA;

(c) Cd : 0.78nm (87 ng 1^{-1}) gives a peak height of 3.5nA;
Pb : 1.36nM (282 ng 1^{-1}) gives a peak height of 4.9nA;

(for instrumental parameters see Section A9.4)

A1.9 Bias

No bias was detected except when interferences occurred.

A1.10 Interferences

Certain substances cause interferences in both Cd and Pb determinations. (See section A3)

A1.11 Time required for analysis

The typical time required for the analysis of one sample, including two standards is approximately 2 hours 40 minutes (when a preconcentration time of 5 minutes is used). This consists of 2 hours UV irradiation of the sample, 5 minutes operator time, 10 minutes initial purging time, and approximately 25 minutes plating and scanning for the sample and two standard additions, including 1 minute purging times between each preconcentration/scan and the next.

Note (a) The range of application and upper limit of linearity are considerably higher than the values quoted; however, when working at elevated concentrations there is a serious risk of contamination of cell components which could cause problems with subsequent analyses at much lower metal levels.

(b) UV irradiated redistilled water, spiked with required standards.

(c) UV irradiated, filtered and metal 'free' sea water, spiked with required standards.

(d) Data obtained at the Department of Oceanography, University of Liverpool.

A2 Principle

A2.1 The method is based upon the preconcentration of amalgam forming metals by plating, in this instance Cd and Pb, by electrodeposition on a hanging mercury drop at a controlled potential of -1.1 V vs a calomel reference electrode. The preconcentration is carried out over an accurately measured time period and the sample solution is stirred at a controlled rate throughout. Preconcentration, or Plating, is followed by the analysis step in which the metal is stripped (oxidised) from the mercury using a linear potential ramp with pulses superimposed and the stripping current is measured. The sensitivity of the determination can be increased, and the detection limit lowered, by increasing the plating time (see section A13).

A2.2 Prior to analysis the sample is passed through a 0.45 μm membrane filter (see section A8.1) to remove particulate material, and subsequently subjected to UV irradiation to destroy organic material. UV irradiation is necessary to

(i) release metals bound up with dissolved organic material,

(ii) destroy surface active organic material which can cause interferences during the subsequent analysis (see section A3).

A2.3 The sample is acidified to approximately pH2.8 in order to ensure that the metals of interest are present in an ionic form; eg by dissolution of colloidal material which has passed through the filter.

A2.4 Prior to the preconcentration step, the sample is purged with argon (or nitrogen) for 10 minutes in order to remove oxygen which causes interference (see section A3). Thereafter it is purged for one minute prior to measurements of internal standards added to the sample.

A2.5 With the present instrumental parameters (see section A9.5) the sensitivity of the technique is directly dependent on the deposition current, defined by the following equation:

Deposition current $i_D = nFD_MC°M/d_M$

Where n = number of electrons involved in the oxidation step (2 for divalent species)

F = Faraday
D_M = diffusion rate of metal ion M
$C°_M$ = concentration of M in sample solution
d_M = diffusion layer thickness

d_M is determined by the stirring rate and is constant for a fixed stirring rate. D_M is temperature dependent, increasing by 3% per °C. Care must be taken that the temperature is constant to at least ± 0.5° C during a set of measurements, to ensure that variations in D_M, and hence in deposition current and peak height, are < 1.5%. No special precautions need to be taken if the sample is at room temperature.

A2.6 Following the preconcentration step, the stirrer is switched off and a period of 30s is allowed to lapse before stripping is initiated. This is to

(i) allow the sample solution to come to rest (at least 10s) and

(ii) ensure that the metal is evenly distributed throughout the Hg drop.

A2.7 Following a waiting time of 30s a potential ramp of 10 mVs^{-1} is applied, with pulses (5 s^{-1}) superimposed on the ramp. The current is sampled and the output is obtained in the form of peaks, with heights proportional to the amount of electroactive species formed in the preconcentration step. The Cd peak is at a potential of −0.65 V in sea water and −0.60 V in redistilled water. The Pb peak is at a potential of −0.44 V in sea water and −0.41 V in redistilled water. All peak potentials quoted are vs a standard calomel electrode (SCE), and at a pH of 2.8 ± 0.2.

A2.8 The concentrations of Cd and Pb in the samples are determined by the method of standard additions.

A3 Interferences

A3.1 Oxygen, surface active organic material, nitrite ion and certain trace metals may all cause interferences in this determination. However, oxygen is removed by purging the sample with an inert gas such as argon or nitrogen. The effects of the remaining substances are shown in tables 1 and 2 and figure 1.

A3.2 Surface active organic material, both natural and synthetic, may interfere as a result of the formation of a film on the Hanging Mercury Drop Electrode (HMDE) surface. The organic film may then slow the rate of metal deposition at the electrode or change the reversibility of the reaction, resulting in a lower peak current, broader peaks or a shift in peak potential to more positive values. The effect of three surface active organic materials is shown in table 1 and figure 1. UV irradiation of a sample at a pH of 2.8 ± 0.2 is sufficient to destroy surface active organic interferents.

A3.3 Metals can interfere in two ways:

(i) as a result of overlapping stripping peaks and

(ii) by intermetallic compound formation

A3.3.1 Overlapping stripping peaks arise when other elements present in the sample (eg Sb, Sn, Tl, In, Cu and Ge) have oxidation potentials close to those of Cd and Pb. Their effects (if any) at concentrations considerably higher than natural ones are shown in table 2.

A3.3.2 No interferences, resulting in changes in the size or position of peak currents, have been found for the following metals at the following concentrations, either singly or cumulatively; 1×10^{-7} M Cr, 2×10^{-7} M Ni, 8×10^{-8} M Zn, 9×10^{-8} M Co, 5×10^{-8} M V, 2×10^{-7} M Mn, 2×10^{-7} M Fe, 1×10^{-7} M Mo, at Cd and Pb concentrations of 7 and 8×10^{-9} M respectively.

A3.3.3 A further form of interference may result from measurement of low concentrations of Cd in a sample containing high concentration of Pb since the lower, negative potential portion of the Pb peak may overlap the much smaller Cd peak. This will also be true for the opposite situation: high Cd concentration, low Pb concentration. This effect has been investigated for a 100-fold increase in Pb concentration

over Cd concentration (and vice versa) and no change in the Cd (or Pb) peak height was found.

A3.4 Nitrite NO_2^-, does not interfere when present at concentrations of up to 4×10^{-5} M.

A4 Hazards

A4.1 Mercury

Mercury is toxic by inhalation and its effects as a poison are cumulative. Great care should therefore be taken in handling it; mercury should be stored in a sealed container and waste mercury should be kept under water. Apparatus containing mercury should be stored in a safety tray. Spillage must be collected at once in order to protect both staff health and electronic circuitry. Mercury and its vapour alloy with many metals especially copper, silver and gold, also clean aluminium which then corrodes rapidly. It has been suggested that covering working areas with siliconized release paper helps to minimize the scatter of spilled mercury (64).

A5 Reagents

A5.1 Redistilled Water

The redistilled water used in the preparation of 50% HCl, 0.1 N HNO_3, for determinations of Cd and Pb, and for rinsing apparatus can best be obtained from a double silica still. The organic content of this water is generally less than that produced by deionizers.

A5.2 50% (v/v) Hydrochloric Acid

Dilute 10 ml of ultrapure HCl to 20 ml by addition of redistilled water. It is prepared freshly, weekly, and it is stored in a polyethylene or polystyrene bottle; prolonged storage can lead to the introduction of organic interferents when this reagent is used to acidify the sample.

A5.3 1 N Nitric Acid

Dilute 60 ml of ultrapure, 16.6 N nitric acid to 1 l by addition of redistilled water. This solution is used in the preparation of 1,000 ppm stock solutions.

A5.4 0.1 N Nitric or Hydrochloric Acid

Dilute 3 ml of ultrapure, 16.6 N nitric acid, or 4.4 ml of ultrapure, 11.4 N hydrochloric acid to 500 ml by addition of redistilled water. It is stored in a polyethylene container and is used in the preparation of working standard solutions.

A5.5 1 N Nitric or Hydrochloric Acid

Reagent grade nitric or hydrochloric acid is diluted to 1 N with distilled water and is used to acid wash and soak the cell, cell components, glass pipettes etc.

A5.6 Standard Cd and Pb Solutions

A5.6.1 Cadmium, 8.9×10^{-3} M (1,000 ppm)

Dissolve 1.000 ± 0.002 g of cadmium in 20.0 ± 0.1 ml of nitric acid (1 N), transfer the solution to a 1 l calibrated flask and dilute to the mark with 1 N HNO_3. Store the solution in a clean polyethylene bottle. Suitable working Cd standards are prepared from the above solution by dilution with 0.1 N redistilled nitric acid and are stored in clean polyethylene bottles. The more dilute Cd standards are best prepared afresh each day.

A5.6.2 Lead, 4.83×10^{-3} M (1,000 ppm)

Dissolve 1.599 ± 0.002 g of Pb $(NO_3)_2$ in 20.0 ± 0.1 ml of nitric acid (1 N), transfer the solution to a 1 l calibrated flask and dilute to the mark with 1 N HNO_3. Store the solution in a clean polyethylene bottle, it is stable indefinitely. Suitable working Pb standards are prepared from the above solution by dilution with 0.1 N redistilled nitric acid and are stored in clean polyethylene bottles. The more dilute Pb standards are best prepared afresh each day.

A5.7 Mercury

Triple-distilled mercury, usually obtained commercially is used to fill the reservoir of the working electrode. Special vacuum mercury stills are available but require adequate containment and ventilation as well as mercury proof pumps. Such stills need to be secured firmly as bumping can be severe. This reagent is hazardous (see section A4).

A5.8 Saturated Potassium Chloride Solution

Shake 25 g of high purity potassium chloride with 45 ± 1 ml of redistilled water until equilibrium is obtained. Use this solution to fill the salt bridge of the calomel reference electrode.

A5.9 Manganese Dioxide Suspension

Dissolve 0.8 g NaOH in 50 ml of redistilled water and dissolve in this solution 1.58 g $KMnO_4$. Dissolve 3.96 g $MnCl_2$. $4H_2O$ in 100 ml redistilled water. Transfer 75 ml of this solution to a centrifuge tube, place a magnetic stirrer bar in the solution and insert a pH electrode. Switch on the stirrer and slowly add 50 ml of $KMnO_4$/NaOH solution. Simultaneously increase the stirring rate to prevent the formation of large lumps of MnO_2. Adjust the pH to 5.0 ± 0.2 using 2 M NaOH; centrifuge at 4,000 rpm for 30 minutes and then pour off the supernatant liquid. Resuspend the MNO_2 in redistilled water, adjust the pH to 5.0 ± 0.2 and repeat the centrifugation etc 3 times. After the final centrifugation resuspend the MnO_2 in redistilled water, transfer to a calibrated flask and dilute to 500 ml with redistilled water; this gives an MnO_2 concentration of approximately 0.05 M.

A5.10 Trace Metal Free Sea Water

Prepare by addition of sufficient 'MnO_2' suspension (A5.9) to a sea water sample to give a concentration of 10^{-4} M. The mixture is then shaken overnight, filtered, subjected to UV irradiation and stored in a clean PTFE or fused silica container in which it is stable for up to 6 days.

A5.11 Redistilled Water

Prior to the analysis, redistilled water is drawn from a double silica still and subjected to UV irradiation for 2–3 hours in cleaned silica tubes. Store in a clean PTFE or fused silica container for up to 6 days.

A6 Equipment

A6.1 Cleanliness

Where possible, plastic and glassware should be reserved solely for low level Cd and Pb determinations. Clean all glassware by standing it in 1 N nitric or hydrochloric acid, when not in use and before use wash it with redistilled water several times. Stand the platinum counter electrode, the magnetic stirrer bar and the PTFE bubbling tube in 1 N acid when not in use; before use rinse thoroughly with redistilled water. Stand the calomel reference electrode in 3 M KCl solution, which has been acidified to approximately 0.1 N with 50% (v/v) hydrochloric acid when not in use, and rinse thoroughly with redistilled water prior to use. After the measurement of each sample rinse the outside of the working electrode glass capillary tube with redistilled water and after use store it either dry (cover it) or in distilled water.

A6.2 Hanging Mercury Drop Electrode (HMDE)

A6.3 50 ml Glass Electrochemical Cell plus fitted polyethylene lid with apertures for working electrode, reference electrode, pH electrode (optional), counter electrode and purge gas bubbler.

A6.4 Standard Calomel (reference) Electrode (SCE). The reference electrode is filled with saturated KCl solution to a level such that when the SCE is immersed in the sample solution, the sample solution level is above the level of the KCl solution in the SCE (see figure 2); this is to prevent a net outflow of KCl solution, which might contain significant levels of Cd and Pb, to the sample solution. To avoid this form of contamination the use of a double-junction reference electrode is recommended. The outer sleeve is then filled with 0.1 M KCl or with the sample.

A6.5 Platinum Wire Counter Electrode, 0.46 mm diameter.

A6.6 PTFE Bubbling Tube connected, via a drechsel bottle containing redistilled water, to a cylinder of argon or nitrogen.

A6.7 A suitable Polarographic Analyser

A6.8 A good quality X-Y or Y-time Chart Recorder

A6.9 An electronically controlled Magnetic Stirrer

A6.10 Polycarbonate Pressure Filtration Apparatus for use with 47 mm diameter membrane filters. (The Sartorius apparatus has been found satisfactory).

A6.11 UV Irradiation Chamber fitted with lkW-mercury lamp with concentrically arranged fused silica tubes of about 150 ml capacity. (see fig 28).

A6.12 A Micropipette (or pipettes) variable between 10 μl and 100 μl.

A7 Sample Collection

For the collection of surface water samples use clean, acid washed, plastic containers; for sub-surface collections use an all-plastic sampling apparatus and suspend it by a plastic-coated suspension cable. Care should be taken to avoid the collection of samples either close to the ship or close to the exhaust of an outboard motor. In collecting a river or estuarine sample care should be taken to avoid collecting a non-representative sample (57,58).

A8 Pretreatment and Storage of Samples

Immediately after collection, pass the sample (not less than 500 ml) through a 0.45 μm membrane filter (which has been washed by soaking in 0.1 N nitric acid and then rinsing in redistilled water) using a polycarbonate pressure filtration apparatus and a nitrogen pressure of about 0.3 bar. Acidify 100 ml of the filtered water sample to pH2.8 ± 0.2 by addition of 100 ± 5 μl of 50% (v/v) hydrochloric acid. Irradiate the acidified sample for 2–3 hours in a clean silica tube. Store the irradiated sample in a clean PTFE or fused silica container until analysed.

A9 Analytical Procedure

Read Section 4 on Hazards before starting this procedure.

Step	Procedure
A9.1	Accurately pipette 50 ml of the irradiated sample into the electrochemical cell.
A9.2	Place the cell, and cell components, in position (see figure 2), close the lid securely and gently bubble argon through the solution for 10–15 minutes.
A9.3	Meanwhile, fill the mercury reservoir in the mercury working electrode, ensuring that no air bubbles or moisture are trapped and that minimal oxide film is present on the mercury. Place the electrode in position in the cell and connect it to the polarograph.
A9.4	Set up the polarograph as follows:

Initial potential	−1.1 volts
Modulation (pulse) amplitude	50 mV
Scan rate	10 mVs^{-1} (+ve direction)
Drop time	0.2s
Operating mode	Differential pulse
Low pass filter	Off
Current range	0 − 0.2 μA(a)

(a) note that lower settings than 0.2 μA generally result in steeper base lines, increased noise and hence difficulties in measuring peak heights; higher current range settings should be used if relatively high concentrations of Cd and Pb are expected.

Step	Procedure
A9.5	Once purging of the sample is complete and the polarograph is set up plating may be commenced. A fresh mercury drop is extruded (b) and the magnetic stirrer switched on (c). Once the sample solution is in steady motion the plating is commenced and the timer started. After exactly 5 minutes plating the stirrer is switched off, and after a further 30s waiting period (see section A2.6), during which the chart recorder is activated, the scan is initiated over a current range corresponding to the expected metal concentrations and the peaks are recorded. (b) The Mercury drop used had a volume of 4×10^{-4} cm^3 corresponding to a radius of 0.46 mm. Reproductibility of drop size to more important than the exact size used. (c) The optimum stirring rate, which gives maximum sensitivity without too much turbulence in the sample solution, must be determined experimentally as it will vary with the shape of the electrochemical cell etc.
A9.6	Appropriate standard additions of Cd and Pb are then made to the sample with a micro pipette and the solution purged with argon for a further one minute period. The previous mercury drop is discarded and a further two drops are formed and discarded before the working drop is extruded. Repeat the measurement as described in section A9.5. The volume of the standard additions should be small, ie < 50 µl, so as not to significantly alter the volume of the sample.
A9.7	Further standard additions of Cd and Pb are made and section A9.6 repeated.

A10 Measurement of Peak Heights

A10.1 For Freshwater Samples

Peak heights are usually measured from a drawn base line (see figure 4), however, if this method is used when redistilled water is the sample, a systematic error can be introduced at low (< nM) Cd and Pb concentrations. This is clearly seen by a comparison of a scan (scan 1) after 30s plating with the solution at rest with a scan (scan 2) (for the same solution) after 5 min plating with stirring (plus 30s at rest) (see figure 3). This problem can be overcome by superimposing a tracing of scan 1 over subsequent scans made using the same current range, and using scan 1 as a baseline from which to measure peak heights (see figure 3). If the polarograph is interfaced with a suitable computer then automatic baseline corrections can be made.

A10.2 For sea water samples

The baseline effect described in section 10.1 is not apparent when sea water is the sample, peak heights are therefore measured from a drawn base line (see figure 4).

A10.3 The baseline effect described in section 10.1 is barely apparent at a salinity of 1‰ and not apparent at all at a salinity of 5‰.

A11 Preparation of Calibration Curve

Subtract the sample peak heights from those obtained after addition of standards and then plot peak height vs concentration using zero concentration/zero peak height as a point. The sample concentrations can then be read from the calibration curve.

A12 Sources of Error

The analytical procedure can be applied to samples ranging from ultra-pure water to sea water, but as with most determinations of trace substances, the major source of error is the introduction of contaminants. The ways in which general contamination is avoided vary from laboratory to laboratory, analysts must decide on the precautions appropriate to their requirements. The use of a laminar flow cabinet is recommended.

A12.1 Temperature variations

Temperature variations can affect the diffusion rate of metals into the mercury drop (see section A2.5). Under conditions used in this method the temperature was constant to within ± 0.5°C during a set of measurements, resulting in variations in the diffusion rate, and hence of the peak heights, of about 1.5%.

A12.2 Measurements of peak heights

Due to imprecision in the drawing of base lines, thickness of lines etc, these measurements are somewhat subjective and hence are liable to operator errors, particularly for small peak heights. Errors also tend to be higher when a very high sensitivity (low current range) is used because of increased instrumental noise.

Experienced operators find that it is helpful to reconstitute the base line as it would be for zero or low concentrations of metal. This may be simulated by repeating determinations using shorter deposition times and superimposing these on the plot to be measured. However modern computerized equipment can produce reproducible data.

A12.3 Introduction of contaminants via apparatus and reagents used

Contaminants can be introduced to the sample in two main ways.

A12.3.1 Leakage of contaminants into solution

Contaminants can leak into the solution from cell components, eg glass cell walls, the platinum electrode, or from the solution in the salt bridge of the reference electrode. This form of contamination manifests itself as successive increases in peak height when a series of replicate platings and scans is carried out on the same solution; all other conditions ie temperature, stirring rate, plating time etc, being constant. This type of contamination can be avoided by leaving the cell components to soak in acid when they are not in use and in the case of the reference cell using it in the manner described in section A6.4.

A12.3.2 Contaminants associated with reagents and standards

The second form of contamination is from the reagents used; taking into account the high quality reagents that are available this is not likely to be a significant factor.

A12.4 Interfering substances

See section A3.

A13 Effect of Preconcentration (or plating) Time

A fixed preconcentration or plating time of 5 minutes has been used in the method as given, however, this can be varied. Generally, doubling the plating time increases the sensitivity by the same factor, and hence halves the detection limit. If the plating time for the same solution is increased stepwise an approximately linear response is obtained (at sub nM levels of Cd and Pb) up to a plating time of 20 minutes; with longer times than this, linearity begins to fall away appreciably (see figure 5).

A14 Checking the Accuracy of Analytical Results

Once the method has been put into routine use the main factor which will affect the accuracy of results (apart from contamination) will be operator errors, eg pipetting, peak height measurement etc. The effect of this was assessed by the determination, on six successive days, of Cd and Pb in a spiked, UV irradiated, sea water sample. The mean concentrations and standard deviations are presented here:

	Cd	Pb
Mean concentration	: 4.35×10^{-9} M	6.80×10^{-9} M
Standard deviation	: 0.079×10^{-9} M	0.197×10^{-9} M
% standard deviation	: 1.8	2.8

These values are comparable with those obtained from replicate scans on the same solution (see section A1.6).

(Data obtained at the Department of Oceanography, University of Liverpool).

Table 1

The effect of surface active organic material on Cd and Pb peak currents

		Peak heights, nA (and peak potentials, volts)	
(a)	Triton-X-100 concentrations, mgl^{-1}	Cd (2.2×10^{-8} M)	Pb (2.5×10^{-8} M)
	0.0	76.6 (−0.645 V)	88.2 (−0.437 V)
	0.2	15.2 (−0.625 V)	84.2 (−0.437 V)
	0.4	9.0 (−0.610 V)	81.7 (−0.437 V)
	1.0	4.7 (−0.585 V)	77.2 (−0.437 V)
	2.0	1.6 (−0.555 V)	65.7 (−0.437 V)
	5.0	— —	41.5 (−0.428 V)
(b)	Sodium lauryl sulphate concentration, mgl^{-1}		
	0.0	78.7	94.0
	0.2	72.5	87.0
	0.4	74.5	91.5
	1.0	67.7	92.0
	2.0	41.5	91.0
	5.0	41.0	90.0
(c)	Cetyl pyridinium bromide concentration, mgl^{-1}		
	0.0	80.5	95.0
	0.2	49.7	92.0
	0.4	38.2	87.0
	1.0	10.5	15.0
	2.0	9.5	9.5
	5.0	9.5	7.5

Table 2

The effects of Sb, Sn, Tl, In, Cu and Ge on the peak currents of Cd and Pb at Cd and Pb concentrations of 7 and 8×10^{-9} M respectively (The effects are expressed as a percentage of the original peak heights before an addition of the potential interferant is made).

Potential Interferant	Concentration of potential interferant	Percentage effect on peak-height	
		Cd	Pb
Sb	up to 33×10^{-9} M	—	—
Sn	up to 34×10^{-9} M	—	—
Tl	up to 4×10^{-9} M	—	—
Tl	8×10^{-9} M	−7%	—
In	9×10^{-9} M	+12%	—
In	17×10^{-9} M	+44%	—
Cu	up to 8×10^{-8} M	—	—
Ge	up to 3×10^{-8} M	—	—

Figure 1 Effect of surface material on Cd and Pb peak heights

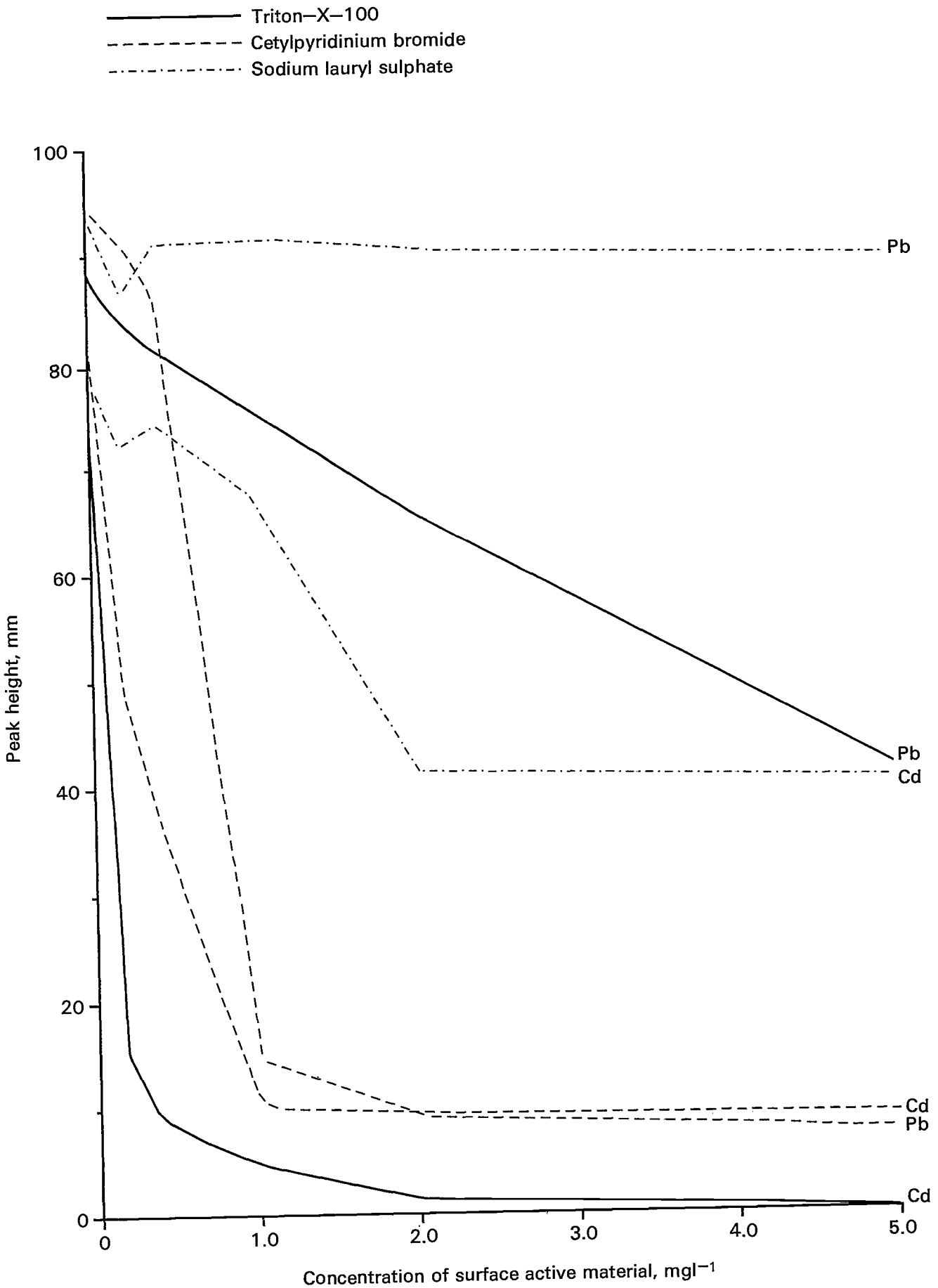


Figure 2 Electrochemical cell and electrode arrangement

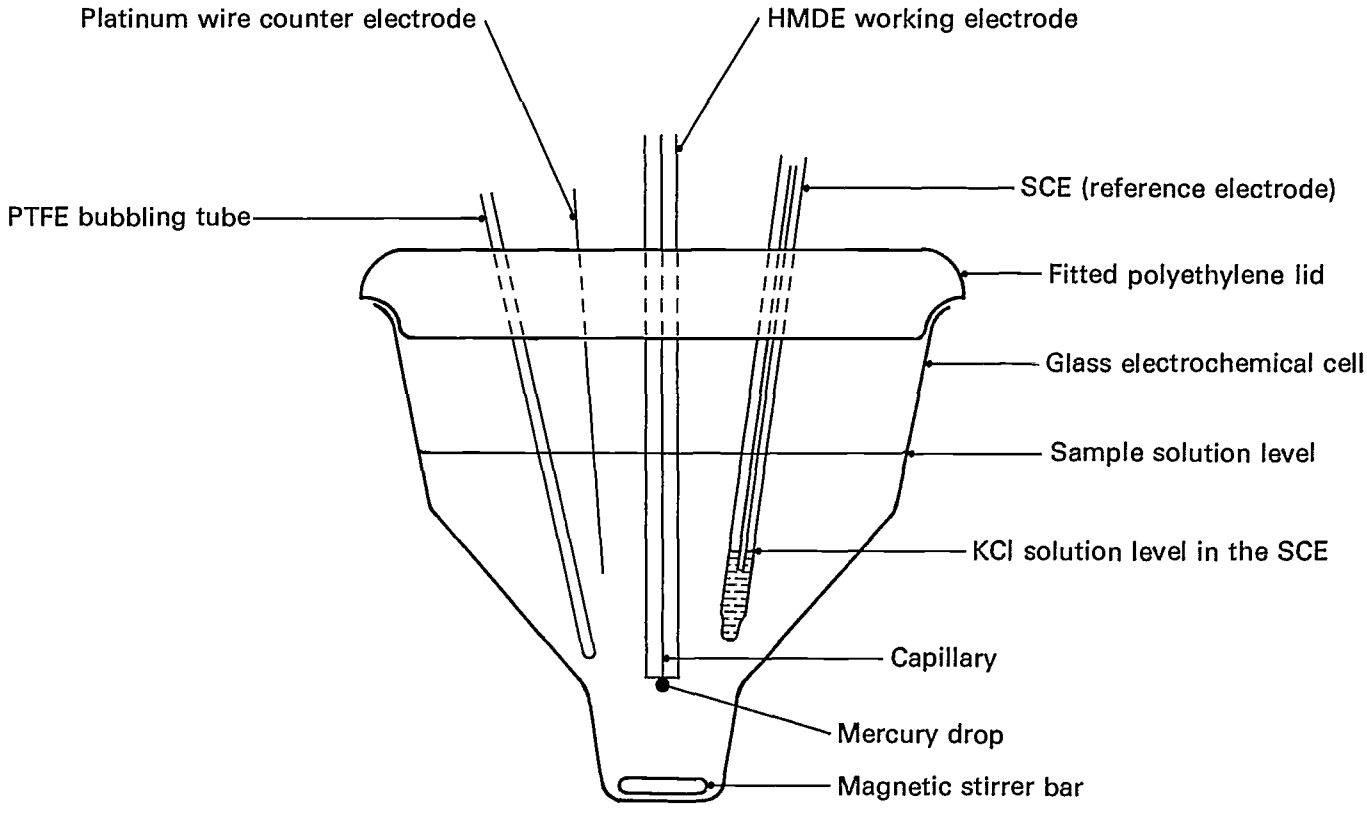


Figure 3 Differential pulse polarography of Cd and Pb

Conditions: redistilled water, pH ~2.8, initial potential −1.1V scan rate 10mV/s, 50mV pulse amplitude, 0.2 μA current range

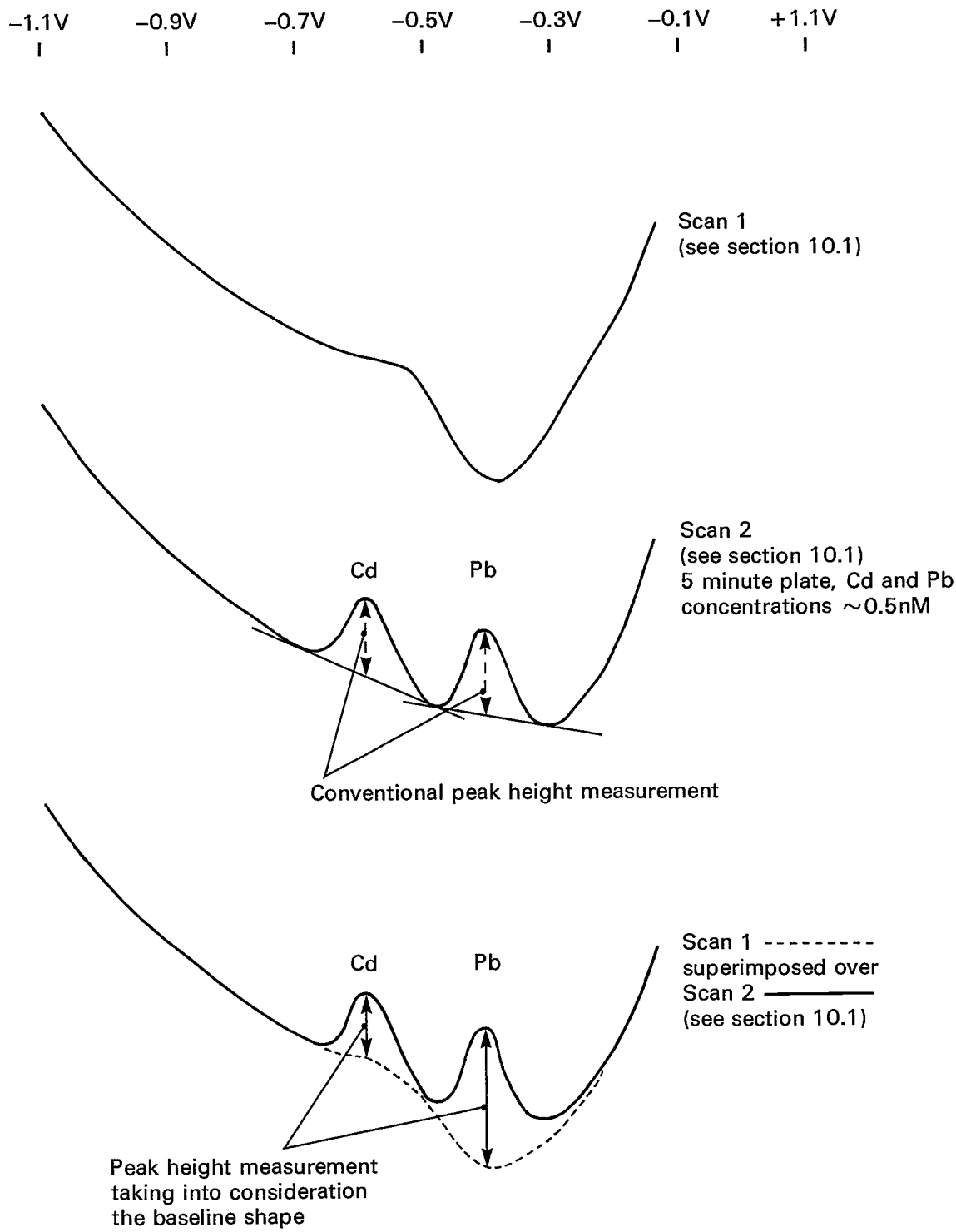


Figure 4 Differential pulse polarography of Cd and Pb

Conditions: sea water, pH ~2.8, initial potential −1.1V, scan rate 10mV/s, 50mV pulse amplitude, 0.2μA current range (for the Cd peak) and 0.5 μA current range (for the pb peak)

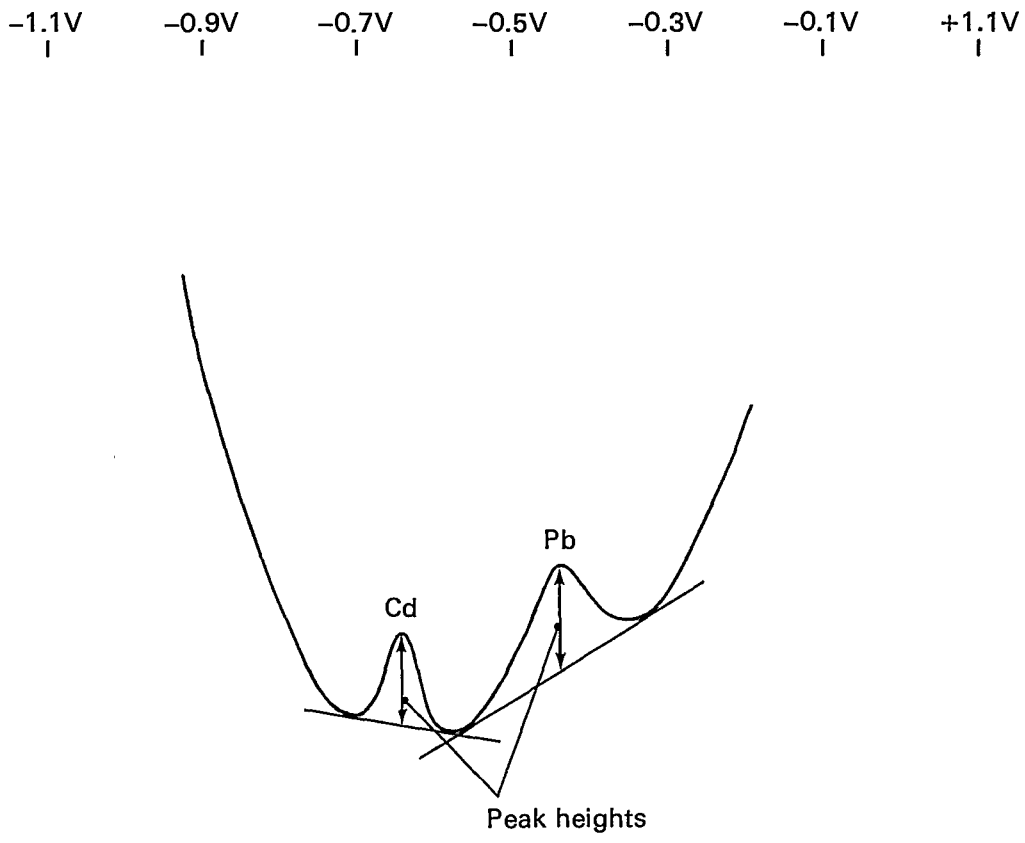
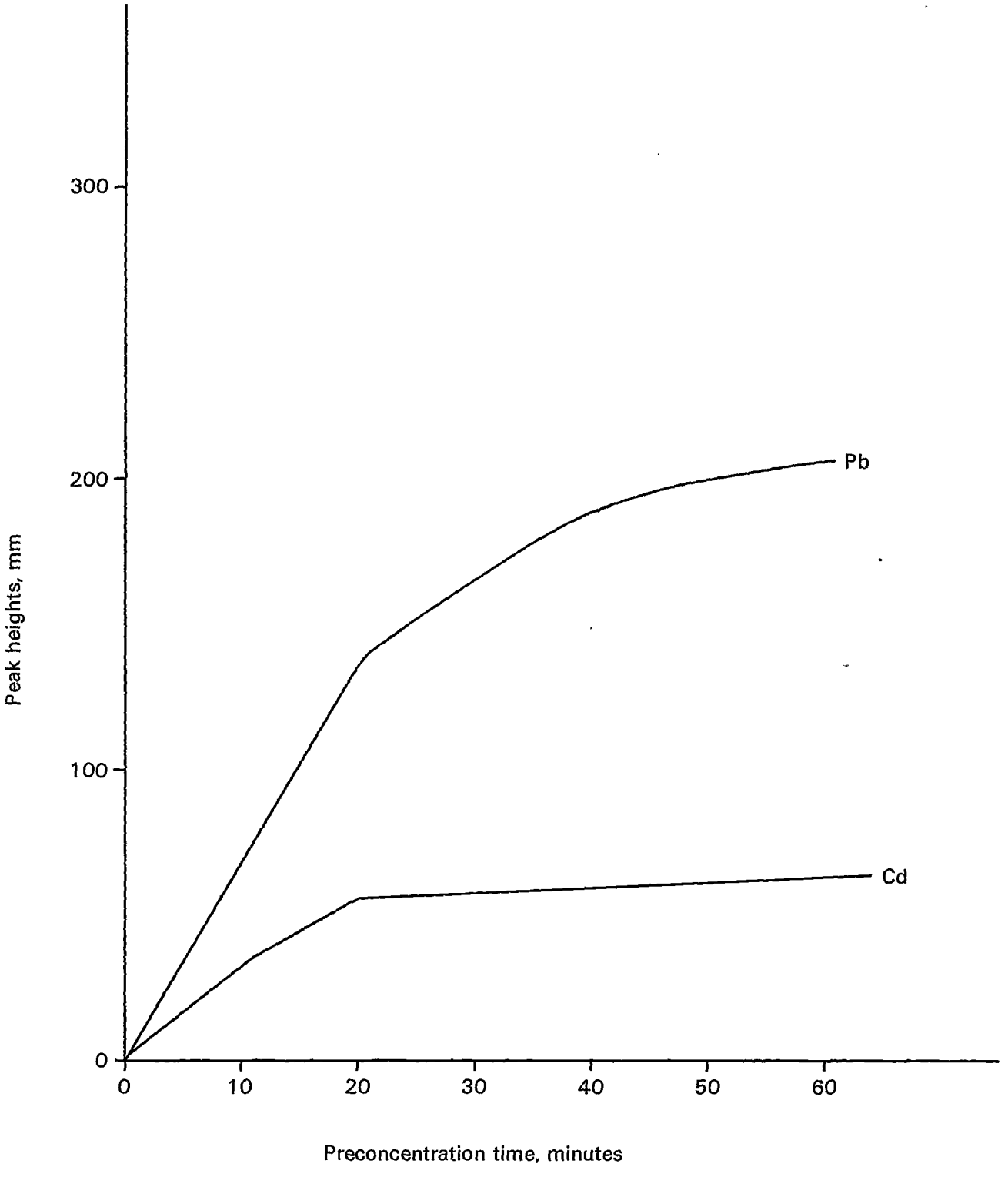


Figure 5 Effect of preconcentration (or plating) time on sensitivity (i.e. peak heights) for Cd and Pb

Conditions: redistilled water, initial potential −1.1V, scan rate 10mV/s, 50mV pulse amplitude, peak heights normalised to 0.2 μA current range, concentrations of Cd and Pb ~0.4nM and ~1.0nM respectively



B Direct Determination of Dissolved Copper in Fresh and Sea Waters by Differential Pulse Cathodic Stripping Voltammetry with the Hanging Mercury Drop Electrode

B1 Performance Characteristics of the method

(For an alternative anode stripping voltammetric method see Ref 71)

B1.1 Substance determined

Dissolved copper in 2^+ oxidation state.

B1.2 Type of sample

Natural and sea waters.

B1.3 Basis of method

The electrodeposition of the complex formed between copper (II) and catechol at the hanging mercury drop electrode (HMDE) surface, and its subsequent determination by differential pulse cathodic stripping voltammetry (DPCSV).

B1.4 Range of application (a)

Up to 10^{-7} M (6.45 $\mu g\ l^{-1}$), (b).

B1.5 Calibration curve (a)

Linearity depends on adsorption time and stirring rate. It is linear up to 1.0×10^{-7} M (6.45 $\mu g\ l^{-1}$) at stated conditions (b).

B1.6 Within Batch Standard deviation (a)

	Copper concentration	Standard Deviation	Degrees of Freedom
(i)	2.0×10^{-10} M (12.7 ng l^{-1})	2.0×10^{-11} M (1.3 ng l^{-1})	10
(ii)	7.3×10^{-9} M (0.46 $\mu g\ l^{-1}$)	1.1×10^{-10} M (7.0 ng l^{-1})	10
(iii)	1.9×10^{-8} M (1.2 $\mu g\ l^{-1}$)	2.4×10^{-10} M (15 ng l^{-1})	6

(i) Redistilled water
(ii) Sea water
(iii) River water

B1.7 Detection limit (a)

6.0×10^{-11} M (3.8 ng l^{-1}), (c).

B1.8 Sensitivity (a)

(i) 7.3×10^{-9} MCu (0.46 $\mu g\ l^{-1}$) gives a peak height of 47 nA
(ii) 8.0×10^{-10} MCu (51.0 ng l^{-1}) gives a peak height of 4.7 nA

(i) UV irradiated sea water, adsorption time of 3 minutes.
(ii) Redistilled water, adsorption time of 3 minutes.

B1.9 Bias

No bias was detected except when interferences occurred.

B1.10 Interferences

Certain substances cause interferences in the determination of copper (see section B3).

B1.11 Time required for analysis

The typical time required for the analysis of one sample, is approximately 25 minutes; this excludes 2 hours for UV irradiation of the sample which is sometimes necessary to oxidize dissolved organic material; included are 6 minutes for purging of the sample and approximately 20 minutes for adsorption and scanning (when a 3 minute adsorption time is used) of the sample and two standard additions. The time varies, however, according to the sample volume used in that larger sample volumes require a longer purging time.

(a) Work carried out at the Department of Oceanography, University of Liverpool.

(b) Several factors can affect the linear response of this determination (see section B3.4.2).

(c) The detection limit can be reduced further by increasing the adsorption time.

B1.12 Additional Test Data

Procedure as above, but sample preserved at pH < 1.5 with hydrochloric acid and pH adjustment at analysis to same pH as given by method. Standard additions used to calibrate were 2 μg/l and 4 μg/l of copper. Samples analysed for 5 days.

		Standard Deviation (μg/l)				
Sample	Found Mean	Within batch	Within batch	Total	Relative	Degree of Freedom
Coastal Sea Water	0.7 μg/l Cu	0.042	0.031	0.052	7%	7
CSW + 3 μg/lCu		0.390	NS	0.390	10%	8

Mean recovery of spike 83 ± 6% (P = 0.05)
(attributable to slight intermittent non linearity of the standard addition)

Data from WRC Medmenham Laboratory

B2 Principle

B2.1 The method is based upon the formation of catechol complexes of copper (II) and their adsorption at the hanging mercury drop electrode (HMDE) at a controlled potential of −0.05 V vs a standard calomel reference electrode. The preconcentration is carried out over an accurately measured time period in a solution which is maintained at pH 7.5 by addition of HEPES buffer and which is stirred at a constant rate throughout. Preconcentration, or adsorption is followed by the analysis step in which the reduction current of the adsorbed complex of copper is measured by differential pulse cathodic stripping voltammetry (DPCSV), in which the complex is reduced from the electrode using a linear potential ramp with pulses superimposed.

B2.2 Prior to analysis the sample is passed through a 0.45 μm membrane filter (see section B8) to remove particulate material, and is subsequently subjected to UV irradiation at a pH of 2.8 ± 0.2. UV irradiation is necessary to:

(i) release copper bound up with dissolved organic material, and

(ii) destroy surface active organic material which can cause interferences (see section B3). Acidification is necessary to prevent loss of metal by adsorption onto the vessel walls during UV irradiation.

B2.3 The sample is brought to neutral pH by addition of ammonia, the HEPES buffer is added to an aliquot for analysis, the mixture is then purged with inert gas (Ar or N_2) in order to remove oxygen which is an interferent. (see section B3). The sample is initially purged for 6 minutes (10 ml sample volume), or for a longer period for larger sample volumes.

B2.4 The complexing agent, catechol, is added and the sample is purged for a further 30s.

B2.5 If all other conditions, (eg instrument settings, stirring rate, pH etc) are kept constant, the sensitivity of the technique is directly dependent on the rate of deposition, which is in turn proportional to the diffusion rate of the complex ion onto the HMDE surface. The diffusion rate is temperature dependent and it is therefore necessary to ensure that the temperature is constant to within ± 0.5°C during a set of measurements. (0.5°C change in temperature results in a variation in the rate of adsorption, and hence in the peak heights, of about 1.5%). No special precautions need to be taken if the sample is at room temperature.

B2.6 Following the adsorption step, the stirrer is switched off and a period of 15s is allowed to elapse, during which the solution comes to rest, before stripping is initiated.

B2.7 Following the waiting time, a potential ramp of 10 mVs^{-1} is applied, with pulses ($10s^{-1}$) superimposed on the ramp. The current is sampled and the output is obtained in the form of peaks, with heights proportional to the amount of electroactive species formed in the preconcentration step. The copper peak is at a potential of approximately −0.20 V vs a SCE at a pH of 7.5

B2.8 The concentration of copper in the sample is determined by the method of standard additions. (See Figure 6).

B3 Interferences

B3.1 Oxygen, surface active organic material, strong chelating compounds and some dissolved metals cause interferences. Oxygen, however, is removed by purging the sample with an inert gas (N_2 or Ar).

B3.2 Surface active organic material reduces the peak current for Cu considerably. The non-ionic surfactant Triton-X-100 has been previously used as a model for surface active organic material in sea water (41), when it was found that suppression of capacitance on a HMDE by surface active organic material in sea water was similar to that caused by 0.01–0.05 mg l^{-1} of Triton-X-100. The effect of additions of Triton-X-100 to UV irradiated sea water on the copper peak is shown in table 3. UV irradiation of a sample at pH 2.8 ± 0.2 is sufficient to destroy surface active organic interferents.

B3.3 High concentrations of strong chelating compounds can mask the Cu peak. In redistilled water, at pH 7.5, with 10^{-4} M catechol and a Cu concentration of 3×10^{-10} M the Cu peak current is completely suppressed by 10^{-3} M EDTA. Natural organic complexing ligands, however, are much weaker complexing agents than EDTA, and are present in natural waters at far lower concentrations than 10^{-3} M. UV irradiation is sufficient to destroy chelating interferents.

B3.4 Other metals can interfere potentially in two ways:

(i) as a result of overlapping stripping peaks

(ii) as a result of competition from other metal-catechol complexes for space on the HMDE surface.

B3.4.1 Overlapping stripping peaks are produced when catechol complexes of other elements present in the sample have reduction potentials close to that of the catechol complex of copper. The following elements at the given concentration do not produce peaks: 10^{-7} M Al (III), Si (IV), Mo (VI), Sn (V) and As (V), and 10^{-8} M Se (VI), Cr (VI), Cd (II), Ga (III), Te (V) and Co (II); conditions used were 4×10^{-4} M catechol, pH 7.0, 3 minute adsorption time in sea water.

Table 4 shows the peak potentials and sensitivities for the metals which do produce peaks. However, at concentrations typical of those in unpolluted sea water, no peaks are produced by Bi, Pb and In, and only very small peaks are produced by Sb, Ni and Zn. The copper peak is followed by that of iron which gives a peak 0.15 V more positive than copper and does not overlap at up to over a 10 fold greater Fe concentration.

B3.4.2 The second form of interference arises from saturation of the HMDE surface and competition for space from other metal-catechol complexes. For a fixed adsorption time this form of interference can affect the linear range of the technique and reduce sensitivity. This interference can be overcome by using an alternative preconcentration step to adsorption. Preconcentration is carried out at a potential of -1.05 V (as opposed to -0.05 V). Metal-catechol complexes are adsorbed onto the mercury drop, however, at this potential Cu is reduced and diffuses into the drop whereas Fe and U (the main competitors) diffuse away back into solution. After a fixed plating time the potential is switched to -0.05 V and stripping is initiated (for a typical analytical procedure see B9.11).

B4 Hazards

B4.1 Mercury

Mercury is toxic by inhalation and its effects as a poison are cumulative. Great care should therefore be taken in its handling and storage; See A4.1

B5 Reagents

B5.1 Redistilled Water

The redistilled water used in the preparation of reagents and for the rinsing of apparatus can best be obtained from a double silica still. The organic content of this water is generally less than that produced by deionizers.

B5.2 50% (v/v) Hydrochloric Acid

Dilute 10 ml of ultrapure, 11.4 N hydrochloric acid to 20 ml by addition of redistilled water. It should be prepared freshly weekly, and stored in a polyethylene container.

B5.3 0.1 N Hydrochloric Acid

Dilute 4.4 ml of ultra pure, 11.4 N hydrochloric acid to 500 ml by addition of redistilled water. It should be stored in a polyethylene container and used in the preparation of working standard solutions.

B5.4 1 N Nitric or Hydrochloric Acid

Reagent grade nitric or hydrochloric acid should be diluted with distilled water and used as an acid wash for soaking the cell, magnetic stirrer, glass pipettes and other glass and plastic ware.

B5.5 Standard Copper Solution

B5.5.1 15.7×10^{-3} M Cu Standard (1,000 ppm),in 1 N HCl

Dissolve 1.000 ± 0.002 g of metallic copper in 20 ml of 30% (v/v) nitric acid in a covered beaker, in a fume cupboard. When dissolution is complete, add 10 ml of concentrated hydrochloric acid and evaporate to small volume on a boiling water bath. Take up the residue in 175 ml of 50% (v/v) hydrochloric acid, transfer the solution to a 1 l calibrated flask and dilute to the mark with redistilled water. Store the solution in a clean polyethylene container. Alternatively, a commercial standard solutions for atomic absorption spectrophometry can be used.

B5.5.2 Suitable working standard solutions are prepared from the above solution by dilution with 0.1 N HCl and are stored in clean polyethylene containers for up to 6 days.

B5.6 Mercury

Triple distilled mercury is used to fill the reservoir of the working electrode. This reagent is hazardous (see section B4).

B5.7 Saturated Potassium Chloride Solution

Shake 25 g of high purity KCl with 45 ± 1 ml of redistilled water until equilibrium is obtained. Use this solution to fill the salt bridge of the calomel reference electrode.

B5.8 1 M (pH 7.5 HEPES Buffer Solution)

Dissolve 4.766 ± 0.01 g high purity N-2-hydroxyethylpiperazine-N¹-2-ethane sulphonic acid (HEPES) in 20 ml 0.5 M ammonia solution (B5.10). Adjust to pH 7.5 by cautious addition of 50% (v/v) hydrochloric acid. Store in a clean polyethylene container.

B5.9 0.2 M Catechol Solution

Dissolve 0.22 g high purity catechol in 10 ml of redistilled water. Catechol is readily oxidized in solution. To prevent this, oxygen is purged from the solution by gently bubbling with an inert gas (Ar or N_2) immediately after dissolution of the catechol. The solution is prepared freshly, daily.

B5.10 0.5 M Ammonia Solution

Dilute 2.8 ml of ultrapure, 18 M ammonia solution to 100 ml by addition of redistilled water. Stored in a polyethylene container and use in the preparation of the HEPES buffer solution.

B6 Equipment

B6.1 Cleanliness

Where possible, plastic and glassware should be reserved solely for low level Cu determinations. Clean all plastic and glass apparatus by standing it in 1 N nitric or hydrochloric acid when not in use, and before use wash it with redistilled water several times. Stand the platinum counter electrode, the magnetic stirrer bar and the PTFE bubbling tube in 1 N acid when not in use and before use, rinse thoroughly with redistilled water. Stand the calomel reference electrode in 3 M KCl solution, which has been acidified to approximately 0.1 N with 50% (v/v) HCl, when not in use and rinse thoroughly with redistilled water prior to use. After the measurement of each sample rinse the outside of the working electrode glass capillary tube with redistilled water and after use store it either dry (covered) or in redistilled water.

B6.2 Hanging Mercury Drop Electrode (HMDE)

B6.3 A suitable Polarographic Analyser

B6.4 A good quality X-Y or Y-time Chart Recorder

B6.5 A glass or PTFE Electrochemical Cell which is either readily incorporated as a part of the electrode assembly or has its own sealable polyethylene lid with apertures for working electrode, reference electrode, purge gas bubbling tube, platinum counter electrode and pH electrode (optional).

B6.6 Standard Calomel (reference) electrode (SCE)

The reference electrode is filled with saturated KCl solution to a level such that when the SCE is immersed in the sample solution, the sample solution level is above the level of the KCl solution in the SCE (see figure 2); this is to prevent a net outflow of KCl solution, which may contain significant concentration of Cu, to the sample solution. To avoid this form of contamination a double-junction reference electrode is recommended. The outer sleeve is then filled with 0.1 M KCl or with the sample.

B6.7 Platinum Wire Counter Electrode

B6.8 PTFE Bubbling Tube connected, via a drechsel bottle containing redistilled water, via a regulator, of a cylinder of inert gas (Ar or N_2).

B6.9 An electronically controlled Magnetic Stirrer

B6.10 A PTFE-coated Magnetic Stirrer Bar

B6.11 A polycarbonate Pressure Filtration Apparatus for use with 47 mm diameter membrane filters (The Sartorius apparatus has been found satisfactory).

B6.12 UV Irradiation Chamber fitted with 1 KW-mercury lamp with concentrically arranged fused silica tubes of 150 ml capacity. (see Fig 28).

B6.13 An Adjustable Micropipette variable between 10 μl and 100 μl.

B6.14 A good quality pH Meter and Glass Combination Electrode

B7 Sample Collection

For the collection of surface water samples use clean, acid-washed plastic containers; for sub-surface collections use all-plastic sampling apparatus and suspend it on plastic-coated suspension cable. Care should be taken to avoid the collection of samples close to a ship or close to the exhaust of an outboard motor. In collecting a river or estuarine sample care should be taken to avoid collecting a non-representative sample.

B8 Pretreatment and Storage of Samples

Immediately after collection, pass the sample (more than 500 ml) through a 0.45 μm membrane filter (which has previously been washed by soaking in 0.1 N hydrochloric acid and rinsing in redistilled water) using a pressure of about 0.3 bar. Acidify 100 ± 5 μl of 50% (V/v) HCl. Irradiate the acidified sample for 2–3 hours in a clean silica tube. Store the irradiated sample in a clean PTFE or fused silica container until analysed.

B9 Analytical Procedure

Read section B4 on hazards before starting this procedure

Step	Procedure
B9.1	Bring 100 ml of the acidified, irradiated sample (see B8) to pH 7.8 ± 0.4 by addition of 75 ± 5 μl of 50% (v/v) ammonia solution.
B9.2	Accurately pipette 10 ml of sample into the electrochemical cell.
B9.3	Using a micropipette, add 100 μl of 1 M HEPES buffer to the sample solution.
B9.4	Place a clean stirrer bar in the cell and put the cell into position on the stand ensuring an airtight seal around the rim.
B9.5	Gently bubble an inert gas (N_2 or Ar) through the sample for 6 minutes (a longer purging time is necessary for larger sample volumes).
B9.6	Set up the polarograph as follows:

Initial potential	−0.05 V
Modulation (pulse) amplitude	25 mV
Scan rate	10 mVs^{-1} (-ve direction)
Drop time	0.1 s
Operating mode	Differential pulse
Low pass filter	Off
Current range	0–0.5 μ A. (a)

(a) Note that lower current range settings than 0.5 μA generally result in increased noise and hence difficulties in measuring peak heights; higher current range settings should be used for higher expected Cu concentrations.

B9.7 Using a micropipette, add 50 μl of 0.1 M catechol solution to the sample and purge for a further 30s.

B9.8 Once purging of the sample is complete and the polarograph is set up commence adsorption. First, switch on the magnetic stirrer and the potentiostat (b) Once the sample solution is in steady motion, commence adsorption by extruding a fresh mercury drop (c) and start the timer. After a fixed adsorption time switch off the stirrer, and after a further 15s waiting period, during which the chart recorder is activated, initiate the scan over a current range corresponding to the expected Cu concentration and record the peak.

Step	Procedure

(b) The optimum stirring rate, which gives maximum sensitivity without too much turbulence in the sample solution, must be determined experimentally as it will vary with the shape of the electrochemical cell etc.

(c) The mercury drop used to obtain the test data had a volume of 3.56×10^{-4} cm^3, a radius of 4.4×10^{-2} cm and a surface area of 2.4×10^{-2} cm^2. Drops of slightly different size would be acceptable provided all drops used during the analysis were identical in size and shape.

B9.9 Then make an appropriate standard addition of Cu to the sample with a micropipette and purge the solution with an inert gas for a one minute period. Discard the previous mercury drop and form and discard a yet further drop before the working drop is extruded. Repeat the measurement as described in section.

B9.8 The volume of each standard addition should be small, ie < 25 µl, so as not to significantly alter the volume of the sample.

B9.10 A further addition of Cu standard is made and section B9.9 repeated.

B9.11 When Fe and U are present at high concentrations they may interfere in this determination (see section B3.4.2), however, this problem can be overcome by adopting the following procedure.

B9.11.1 Proceed through steps B9.1–9.5 as usual.

B9.11.2 Set up the polarograph as in B9.9, except set the initial potential to -1.05 V.

B9.11.3 Add the catechol as in B9.7.

B9.11.4 Once purging of the sample is complete, the catechol added, and the polarograph set up, then plating may be commenced. First the magnetic stirrer and the potentiostat are switched on. Once the sample solution is in steady motion plating is commenced by extruding a fresh drop and the timer is started. After a fixed plating time the stirrer is switched off, a period at 15s is allowed to elapse and the initial potential is then switched to -0.05 V. A further period of 20s is allowed to elapse, during which the recorder is activated, and the scan is initiated over a current range corresponding to the expected Cu concentration and the peak is recorded.

B9.11.5 The remainder of the procedure is as described in B9.9 and B9.10.

B10 Measurement of Peak Heights

The peak heights for the sample and the sample plus standard additions of copper are plotted against the concentrations of added copper standard in the manner illustrated in figure 7. The concentration of copper in the sample is then read from the negative portion of the concentration axis.

B11 Sources of Error

The analytical procedure can be applied to samples ranging from ultra-pure water to sea water, but as with most determinations of trace substances, the major source of error is the introduction of contaminants. The ways in which general contamination is avoided vary from laboratory to laboratory, analysts must decide on the precautions appropriate to their requirements. See Section A12. The use of a laminar flow cabinet is recommended. Leave the cell components to soak in acid when they are not in use; use the reference cell in the manner described in Section B6.6. For known interferences see Section B3.

B12 Effect of Preconcentration (or adsorption) Time

Measurements of the reduction current as a function of the adsorption time, are shown in figure 8. The peak current probably levels out as an increasing area of the drop becomes covered with complex ions of other metals when adsorption times are prolonged (43).

B13 Checking the Accuracy of Analytical Results

Once the method has been put into routine use the main factor which will affect the accuracy of results (apart from contamination) will be operator errors, eg pipetting, peak height measurement etc. The effect of these was assessed by the determination, on six successive days, of Cu in a filtered and UV irradiated trace metal 'free' sea water sample. The mean concentration and standard deviation are presented here:

Mean concentration: 5.68×10^{-9} M Cu

Standard deviation: 0.19×10^{-9} M Cu

% standard deviation: 3.3%

(Data obtained at the Department of Oceanography, University of Liverpool).

Table 3

Effect of Triton-X-100 (non-ionic surfactant) on copper peak in redistilled water; conditions: 5.0×10^{-9} M Cu, pH 7.4, 3 minute adsorption time, 10 mVs^{-1} scan rate, 10 pulses s^{-1}, initial potential −0.05 V, 25 mV pulse amplitude.

Triton-X-100 $^{-1}$ concentration, mg l^{-1}	Effect on Cu peak as a percentage of original peak height
0.1	−2%
0.4	−15%
0.65	−22%
1.15	−31%

Table 4

Peak potentials and sensitivities for DPCSV of complex ions of various elements with catechol in sea water

Element	Peak Potential	Sensitivity, peak height/ concentration (nA/nM)
Cu (II)	−0.23	65.0
Bi (III)	−0.34	1.5
Fe (III)	−0.40	5.6
Pb (II)	−0.48	0.1
U (VI)	−0.56	14.0
In (III)	−0.71	0.5
V (V)	−0.72	5.0
Sb (V)	−0.83	13.0
Ni (II)	−0.86	5.0
Zn (II)	−1.04	0.1

Conditions; 4×10^{-4} M catechol, pH 7.0, 3 minute adsorption time, −0.05 V initial potential, scan rate 5 mVs^{-1} 2 pulses s^{-1}, 25 mV pulse modulation.

Note: The Indium concentration in sea water is in the order of 10^{-12} M and that of Sb is in the order of $10^{-11} - 10^{-10}$ M.

Figure 6 Differential pulse polarography of Cu

Conditions: sea water, pH 7.4, initial potential –0.05V, scan rate 10mV s^{-1}, 25mV pulse amplitude, 10 pulses s^{-1}, 0.5 μA current range

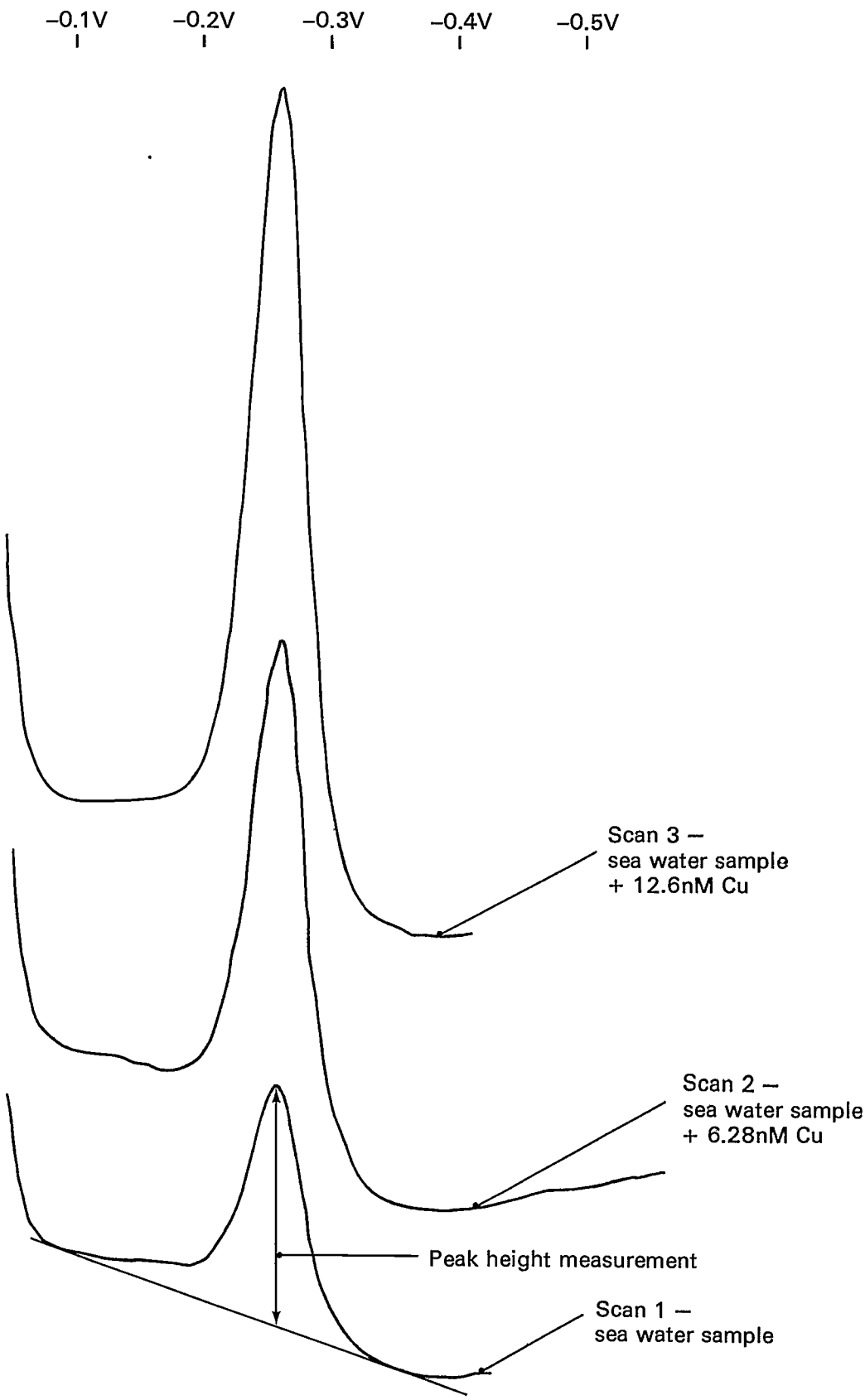
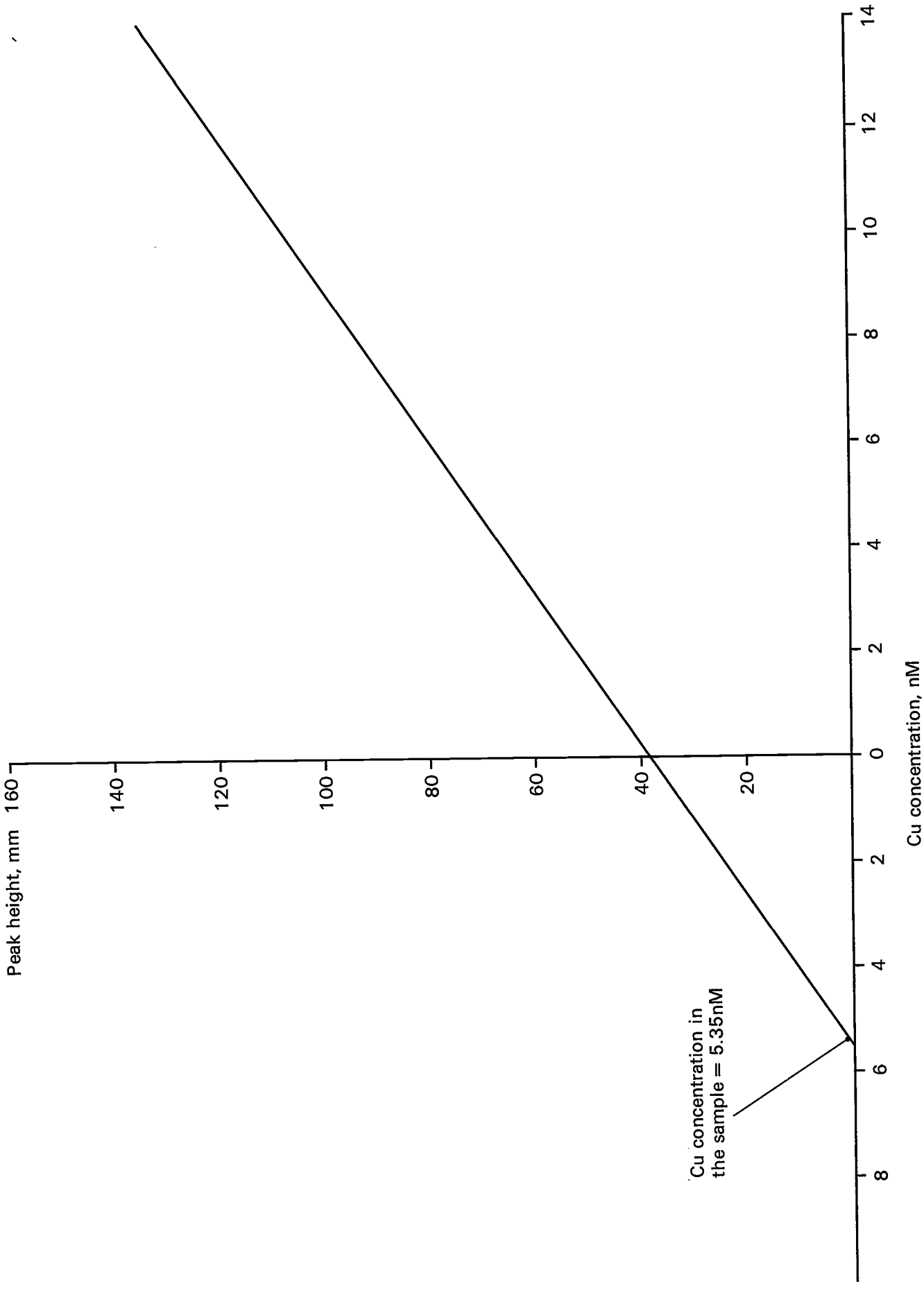


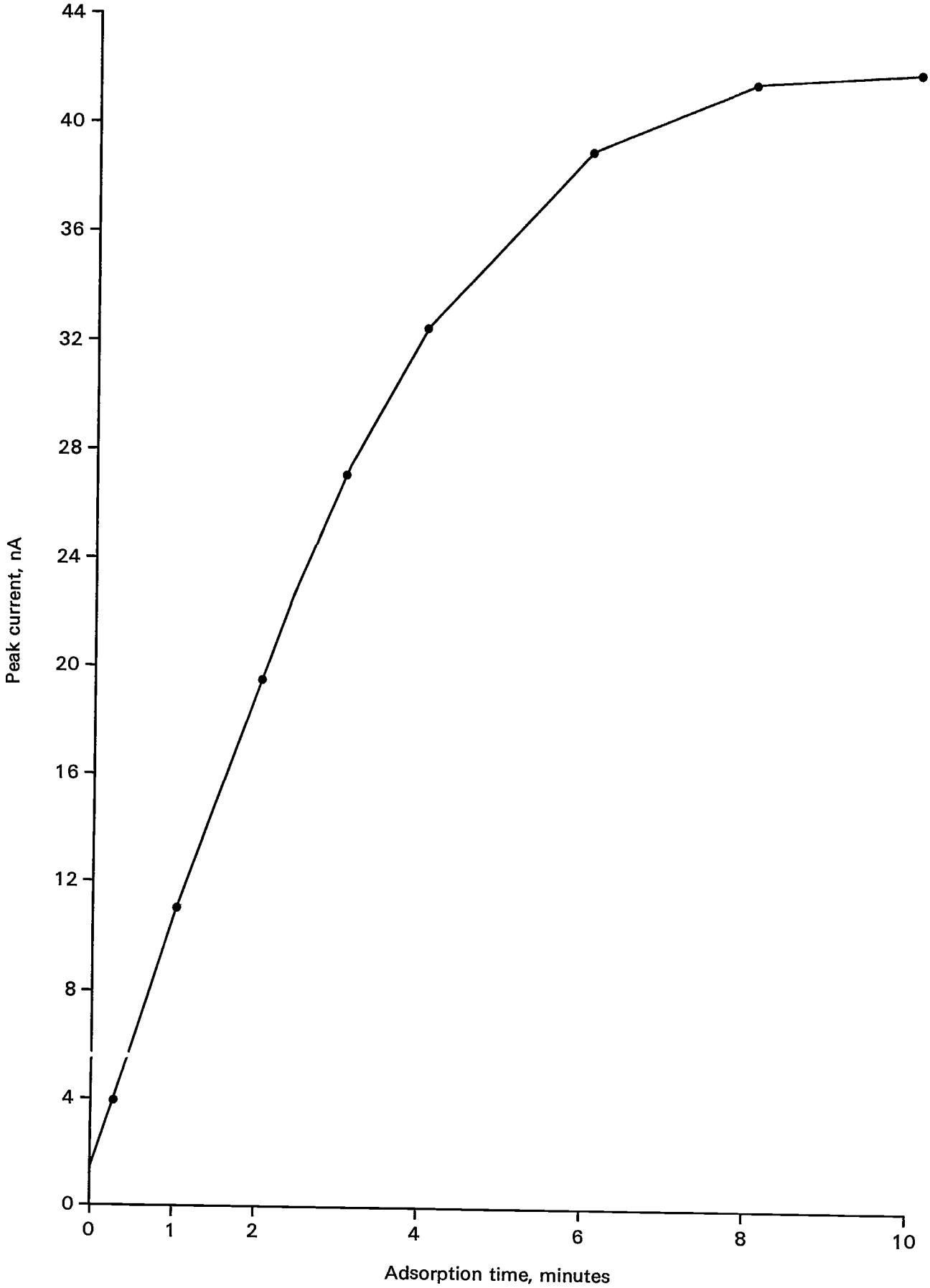
Figure 7 Calibration curve for the determination of Cu



The concentration is given by the intercept with the concentration axis

Figure 8 Effect of preconcentration time on the peak current

Conditions: sea water, initial potential –0.05V, Cu concentration = 8,0nM



C Direct Determination of Dissolved Vanadium in Fresh and Sea Waters by Differential Pulse Cathodic Stripping Voltammetry with the Hanging Mercury Drop Electrode

C1 Performance Characteristics of the method

C1.1 Substance determined

Dissolved vanadium in 5^+ oxidation state.

C1.2 Type of sample

Natural and sea waters.

C1.3 Basis of method

The electrodeposition of the complex formed between vanadium (V) and catechol at the hanging mercury drop electrode (HMDE) surface, and its subsequent determination by differential pulse cathodic stripping voltammetry (DPCSV).

C1.4 Range of application (a)

Up to 10^{-6} M (51 μg l^{-1}, (b).

C1.5 Calibration curve (a)

Linearity depends on adsorption time and stirring rate. It is linear up to 2.0×10^{-7} M (10.2 μg l^{-1} at stated conditions (b).

C1.6 Total Standard deviation (a)

	Vanadium concentration	Standard Deviation	Degrees of Freedom
(i)	3.2×10^{-8} M (1.6 μg l^{-1})	0.7×10^{-9} M (35 ng l^{-1})	8
(ii)	3.0×10^{-9} M (150 ng l^{-1})	1.0×10^{-10} M (5.1 ng l^{-1})	10

(i) UV irradiated sea water
(ii) 0.01 M KC1.

C1.7 Detection limit (a)

3.0×10^{-10} M (15 ng l^{-1}), (c)

C1.8 Sensitivity (a)

(i) 3.2×10^{-8} M V (1.6 μg l^{-1}) gives a peak height of 14.4 nA
(ii) 1.1×10^{-8} M V (550 ng l^{-1}) gives a peak height of 7.3 nA.

C1.9 Bias

No bias was detected except when interferences occurred.

C1.10 Interferences

Certain substances cause interferences in the determination of vanadium (see section C3).

C1.11 Time required for analysis

The typical time required for the analysis of one sample, is approximately 20 minutes; this excludes 2 hours for UV irradiation of the sample which is sometimes necessary to oxidize dissolved organic material; included are 6

minutes for purging of the sample and approximately 10 minutes for adsorption and scanning (when a 1 minute adsorption time is used) of the sample and two standard additions. The time varies, however, according to the sample volume used in that larger sample volumes require a longer purging time.

Note (a) Work carried out at the Department of Oceanography, University of Liverpool

(b) Several factors can affect the linear response of this determination (see section C3.3.2)

(c) The detection limit can be reduced further by increasing the adsorption time until a limit of about 1.0×10^{-10} M V (5.1 ng l^{-1}) is achieved after an adsorption time of 15 minutes.

C2 Principle

C2.1 The method is based upon the formation of catechol compleses of vanadium, (V) and their adsorption at the hanging mercury drop electrode (HMDE) at a controlled potential of -0.1V vs a standard calomel reference electrode. The preconcentration is carried out over an accurately measured time period in a solution which is maintained at pH 6.9 by addition of PIPES buffer and which is stirred at a constant rate throughout. Preconcentration, or adsorption is followed by the analysis step in which the reduction current of the adsorbed complex of vanadium is measured by differential pulse cathodic stripping voltammetry (DPCSV); the complex is reduced from the electrode using a linear potential ramp with pulses superimposed.

C2.2 Prior to analysis the sample is passed through a 0.45 μm membrane filter (see section C8) to remove particulate material, and is subsequently subjected to UV irradiation at a pH of 2.8 ± 0.2. UV irradiation is necessary to:

(i) release vanadium bound up with dissolved organic material, and

(ii) destroy surface active organic material which can cause interferences (see section C3). Acidification is necessary to prevent loss of metal by adsorption onto the vessel walls during UV irradiation.

C2.3 The sample is brought to neutral pH by addition of ammonia, the PIPES buffer is added to an aliquot for analysis, the mixture is then purged with an inert gas (Ar or N_2) in order to remove oxygen which is an interferent. (see section C3). The sample is initially purged for 6 minutes (10 ml sample volume), or a longer period for larger sample volumes, and is thereafter purged for 30s prior to subsequent measurements in the same sample solution.

C2.4 The complexing agent, catechol, is added and the sample is purged for a further 30s.

C2.5 If all other conditions, (eg instrument settings, stirring rate, pH etc) are kept constant, the sensitivity of the technique is directly dependent on the rate of deposition, which is in turn proportional to the diffusion rate of the complex ion onto the HMDE surface. The diffusion rate is temperature dependent and it is therefore necessary to ensure that the temperature is constant to within ± 0.5°C during a set of measurements. This results in variations in the rate of adsorption, and hence in the peak heights, of < 1.5%. No special precautions need to be taken if the sample is at room temperature.

C2.6 Following the adsorption step, the stirrer is switched off and a period of 15s is allowed to elapse, during which the solution comes to rest, before stripping is initiated.

C2.7 Following the waiting time, a potential ramp of 10 mVs^{-1} is applied, with pulses ($10s^{-1}$) superimposed on the ramp. The current is sampled and the output is obtained in the form of peaks, with heights proportional to the amount of electroactive species formed in the preconcentration step. The vanadium peak is at a potential of -0.7 V vs a SCE at a pH of 6.9

C2.8 The concentration of vanadium in the sample is determined by the method of standard additions.

C3 Interferences

C3.1 Oxygen, surface active organic material and some dissolved metals cause interferences. Oxygen, however is removed by purging the sample with an inert gas (N_2 or Ar).

C3.2 Surface active organic material reduces the peak current for V considerably. The non-ionic surfactant Triton-X-100 has been previously used as a model for surface active organic material in sea water (41), and it was found that suppression of capacitance on a HMDE by surface active organic material in sea water was similar to that caused by 0.01–0.05 mg l^{-1} of Triton-X-100. The effect of additions of Triton-X-100 to UV irradiated sea water on the vanadium peak are shown in table 5; UV irradiation of a sample at pH 2.8 ± 0.2 is sufficient to destroy surface active organic interferences.

C3.3 Other metals can potentially interfere in two ways:

(i) as a result of overlapping stripping peaks and

(ii) as a result of competition from other metal-catechol complexes for space on the HMDE surface.

C3.3.1 Overlapping stripping peaks arise when catechol complexes of other elements present in the sample have reduction potentials close to that of the catechol complex of vanadium. The following elements at the following concentrations do not produce peaks:

10^{-7} M Al (III) Si (IV), Mo (VI), Sn (V) and As (V), and 10^{-8} M Se (VI), Cr (VI), Cd (II), Ga (III), Te (VI) and Co (II); conditions used were 4×10^{-4} M catechol, pH 7.0, 3 minute adsorption time in sea water. Table 4 shows the peak potentials and sensitivities for the metals which do produce peaks. However, at concentrations typical of unpolluted sea water no peaks are produced by Bi, Pb and In, and only very small peaks are produced by Sb, Ni and Zn. The vanadium peak is preceded by that of uranium (1.0×10^{-8} M in sea water) which gives a peak about 0.15 V more positive than vanadium and does not overlap up to a 10 fold increase in U concentration.

C3.3.2 The second form of interference arises from saturation of the HMDE surface and competition for space from other metal-catechol complexes. For a fixed adsorption time this form of interference can affect the linear range of the technique. For example for a two minute adsorption time the increase in peak height with vanadium concentration is linear up to 1.0×10^{-7} M V, in the presence of 1.0×10^{-8} M U. In the presence of 5.0×10^{-8} M U there is a loss of linearity at a vanadium concentration of 0.8×10^{-7} M. This loss of linearity can be overcome by reducing the adsorption time and thus preventing saturation of the HMDE surface, since the catechol complex of vanadium then appears to be selectively adsorbed prior to that of uranium.

C4 Hazards

C4.1 Mercury

Mercury is toxic by inhalation and its effects as a poison are cumulative. Great care should therefore be taken in its handling and storage; see A4.1

C5 Reagents

C5.1 Redistilled Water

The redistilled water used in the preparation of reagents and for the rinsing of apparatus can best be obtained from a double silica still. The organic content of this water is generally less than that produced by deionizers.

C5.2 50% (v/v) Hydrochloric Acid

Dilute 10 ml of ultrapure, 11.4 N HCl to 20 ml by addition of redistilled water. Prepare afresh each week, and store in a polyethylene container.

C5.3 0.1 N Hydrochloric Acid

Dilute 4.4 ml of high purity, 11.4 N HCl to 500 ml by addition of redistilled water. It is stored in a polyethylene container and is used in the preparation of working standard solutions.

C5.4 1N Nitric or Hydrochloric Acid

Reagent grade nitric or hydrochloric acid is diluted with distilled water and is used as an acid wash in which to soak the cell, magnetic stirrer, glass pipettes and other glass and plastic ware.

C5.5 Standard Vanadium Solution

C5.5.1 19.6×10^{-3} M V Standard (1,000 ppm), in 1 N HCl

Dissolve 1.000 ± 0.002 g of metallic vanadium in 175 ml of 50% (v/v) HCl, transfer the solution to a 1 litre calibrated flask and dilute to the mark with redistilled water. Store the solution in a clean polyethlyene container. Alternatively, commercial standard solutions for atomic absorption spectrophotometry can be used.

C5.5.2 Suitable working standard solutions are prepared from the above solution by dilution with 0.1 N HCl and are stored in clean polyethylene containers for up to 6 days.

C5.6 Mercury

Triple distilled mercury is used to fill the reservoir of the working electrode. This reagent is hazardous (see section C4).

C5.7 Saturated Potassium Chloride Solution

Shake 25 g of high purity KCl with 45 ± 1 ml of redistilled water until equilibrium is obtained. Use this solution to fill the salt bridge of the calomel reference electrode.

C5.8 1 M (pH7 PIPES Buffer Solution)

Dissolve 6.487 ± 0.002 g high purity piperazine -NN′ -bis-2-ethane sulphonic acid monosodium salt (PIPES) in 20 ml 0.5 M ammonia solution. Adjust to pH 7.0 by cautious addition of 50% (v/v) hydrochloric acid. Store in a clean polyethylene container.

C5.9 0.1 M Catechol Solution

Dissolve 0.22 g high purity catechol in 20 ml redistilled water. Catechol is readily oxidised in solution. To prevent this, oxygen is purged from the solution by gently bubbling with an inert gas (Ar or N_2) immediately after solubilisation of the catechol. The solution is prepared freshly, daily.

C5.10 50% (v/v) Ammonia Solution

Dilute 10 ml of ultrapure, 18 M ammonia solution to 20 ml by addition of redistilled water. It is prepared freshly weekly and is stored in a polyethylene container.

C5.11 0.5 M Ammonia Solution

Dilute 2.8 ml ultrapure, 18 M ammonia solution to 100 ml by addition of redistilled water. The solution is stored in a polyethylene container and is used in the preparation of the PIPES buffer solution.

C6 Equipment

C6.1 Cleanliness

Where possible, plastic and glassware should be reserved solely for low level V determinations. Clean all apparatus by standing it in 1 N nitric or hydrochloric acid when not in use, and before use wash it with redistilled water several times. Stand the platinum counter electrode, the magnetic stirrer bar and the PTFE bubbling tube in

1 N acid when not in use and before use rinse thoroughly with redistilled water. Stand the calomel reference electrode in 3 M KCl solution, which has been acidified to approximately 0.1 N with 50% (v/v) HCl, when not in use and rinse thoroughly with redistilled water prior to use. After the measurement of each sample rinse the outside of the working electrode glass capillary tube with redistilled water and after use store it either dry (cover it) or in redistilled water.

C6.2 A Hanging Mercury Drop Electrode (HMDE).

C6.3 A suitable Polarographic Analyser.

C6.4 A good quality X-Y or Y-time Chart Recorder.

C6.5 A glass or PTFE Electrochemical Cell which is either readily incorporated as a part of the electrode assembly or has its own sealable polyethylene lid with apertures for working electrode, reference electrode, purge gas bubbling tube, platinum counter electrode and pH electrode (optional).

C6.6 Standard Calomel (reference) Electrode (SCE)

The reference electrode is filled with saturated KCl solution to a level such that when the SCE is immersed in the sample solution, the sample solution level is above the level of the KCl solution in the SCE (see figure 2); this is to prevent a net outflow of KCl solution, which may contain significant concentrations of V, to the sample solution. To avoid this form of contamination a double-junction reference electrode is recommended. The outer sleeve is then filled with 0.1 M KCl or with the sample.

C6.7 Platinum Wire Counter Electrode

C6.8 PTFE Bubbling Tube connected, via a drechsel bottle containing redistilled water, to a cylinder of inert gas (Ar or N_2).

C6.9 An electronically controlled Magnetic Stirrer.

C6.10 A PTFE-coated Magnetic Stirrer Bar.

C6.11 A polycarbonate Pressure Filtration Apparatus for use with 47 mm diameter membrane filters. (The Sartorius apparatus has been found satisfactory).

C6.12 UV Irradiation Chamber fitted with 1 kW-mercury lamp with concentrically arranged fused silica tubes of 150 ml capacity. (see fig 28).

C6.13 An Adjustable Micropipette variable between 10 μl and 100μl.

C6.14 A good quality pH Meter and Glass Combination Electrode.

C7 Sample Collection

For the collection of surface water samples use clean, acid-washed plastic containers; for sub-surface collections use all-plastic sampling apparatus and suspend it on plastic-coated suspension cable. Care should be taken to avoid the collection of samples close to a ship or close to the exhaust of an outboard motor. In collecting a river or estuarine sample care should be taken to avoid collecting a non-representative sample.

C8 Pretreatment and Storage of Sample

Immediately after collection, pass the sample (>500 ml) through a 0.45 μm membrane filter, which has been washed by soaking in 0.1 N hydrochloric acid and rinsing in redistilled water, using a polycarbonate pressure filtration apparatus and an inert gas pressure of about 0.3 bar. Acidify 100 ml of the filtered water sample to pH 2.8 ± 0.2 by addition of 100 ± 5 μl of 50% (v/v) HCl. Irradiate the acidified sample for 2–3 hours in a clean silica tube. Store the irradiated sample in a clean PTFE or fused silica container until analysed.

C9 Analytical Procedure Read section 4 on hazards before starting this procedure

Step	Procedure
C9.1	Bring 100 ml of the acidified, irradiated sample to neutral pH (7.8 ± 0.4) by addition of 75 ± 5 μl of 50% (v/v) ammonia solution.
C9.2	Accurately pipette 10 ml of sample into the electrochemical cell.
C9.3	Using a micropipette, add 100 μl of 1 M PIPES buffer to the sample solution.
C9.4	Place a clean stirrer bar in the cell and put the cell into position, ensuring an airtight seal around the rim.
C9.5	Gently bubble an inert gas (N_2 or Ar) through the sample for 6 minutes (a longer purging time is necessary for larger sample volumes).
C9.6	Meanwhile set up the polarograph as follows:

Initial potential	−0.1 V
Modulation (pulse) amplitude	50 mV
Scan rate	10 mV S^{-1} (−ve direction)
Drop time	0.1 s
Operating mode	Differential pulse
Low pass filter	Off
Current range	0–0.5 μA. (a)

(a) note that lower current range settings than 0.5 μA generally result in increased noise and hence difficulties in measuring peak heights; higher current range settings should be used for higher expected V concentrations.

C9.7 Using a micropipette, add 20 μl of 0.1 M catechol solution to the sample and purge for a further 30 s.

C9.8 Once purging of the sample is complete and the polarograph is set up adsorption may be commenced. First the magnetic stirrer and the potentiostat are switched on (b). Once the sample solution is in steady motion adsorption is commenced by extruding a fresh mercury drop (c) and the timer is started. After a fixed adsorption time the stirrer is switched off, and after a further 15 s waiting period, during which the chart recorder is activated, the scan is initiated over a current range corresponding to the expected V concentration and the peak is recorded.

(b) The optimum stirring rate, which gives maximum sensitivity without too much turbulence in the sample solution, must be determined experimentally as it will vary with the shape of the electrochemical cell etc

(c) The mercury drop used when obtaining the test data had a volume of 3.56×10^{-4} cm^3, a radius of 4.4×10^{-2} cm and a surface area of 2.4×10^{-2} cm^2. Drops of slightly different size would be acceptable provided all drops used during the analysis are identical in size and shape.

C9.9 An appropriate standard addition of V is then made to the sample with a micropipette and the solution purged with an inert gas for a one minute period. The previous mercury drop is discarded and a further drop is formed and discarded before the working drop is extruded. Repeat the measurement as described in section C9.8. The volume of each standard addition should be small ie <25 μl, so as not to significantly alter the volume of the sample.

C9.10 A further addition of V standard is made and section C9.9 repeated.

C10 Measurement of Peak Heights

Peak heights are measured from a drawn base line (see figure 9). However, if the polarograph is interfaced with a suitable computer this allows accurate and convenient measurements of peak heights (or peak areas) to be made.

C11 Preparation of Calibration Curve

The peak heights for the sample and the sample plus standard additions of vanadium are plotted against the concentrations of added vanadium standard in the manner illustrated in figure 10. The concentration of vanadium in the sample is then read from the negative portion of the concentration axis.

C12 Sources of Error

The analytical procedure can be applied to samples ranging from ultra-pure water to sea water, but as with most determinations of trace substances, the major source of error is the introduction of contaminants. The ways in which general contamination is avoided vary from laboratory to laboratory, analysts must decide on the precautions appropriate to their requirements. See section A12. The use of a laminar flow cabinet is recommended. Leave the cell components to soak in acid when they are not in use; use the reference cell in the manner described in Section C6.6.

For known interferences see Section C3.

C13 Effect of Preconcentration (or plating) Time

Measurements of the reduction current as a function of the plating time, all other conditions being constant, are shown in figure 11 at two vanadium concentrations. The current was measured by linear scan CSV using a scan rate of 50 mVs^{-1}. At a vanadium concentration of 4.0×10^{-8} M the increase in peak current with plating time is linear up to about 3 minutes and at a vanadium concentration of 1.0×10^{-7} M is linear up to about 1 minute. Furthermore, at the higher vanadium concentration, 1.0×10^{-7} M, a maximum of 210 nA is reached after a 3 minute plating time, after which the peak current decreases. This decrease is due to the competitive adsorption of complexes of copper and uranium which apparently occupy about 30% of the HMDE surface after a collection period of 3 minutes (44).

C14 Checking the Accuracy of Analytical Results

Once the method has been put into routine use the main factor which will affect the accuracy of results (apart from contamination) will be operator errors, eg pipetting, peak height measurement etc. The effect of these was assessed by the determination, on six successive days, of V in a filtered and UV irradiated trace metal 'free' sea water sample. The mean concentration and standard deviation are presented here:

Mean concentration	1.44×10^{-8} M
Standard deviation	0.05×10^{-8} M
% standard deviation	3.6%

(Data obtained at the Department of Oceanography, University of Liverpool).

Table 5.

Effect of Triton-X-100 (non-ionic surfactant) on vanadium peak in sea water; conditions: 3.0×10^{-8} MV, pH 6.9, 1 minute adsorption time, 19 mVs^{-1} scan rate, 10 pulses s^{-1}, initial potential −0.1 V, 25 mV pulse amplitude.

Triton-X-100 Concentration, mg l^{-1}	Effect of V peak as a percentage of original peak height
0.5	−12%
1.0	−60%
2.0	−100%

Figure 9 Differential pulse polarography of vanadium

Conditions: sea water, pH 6.9, initial potential −0.1V, scan rate 10mV/s, 25mV pulse amplitude, 5 pulses/s, 0.5 μA current range

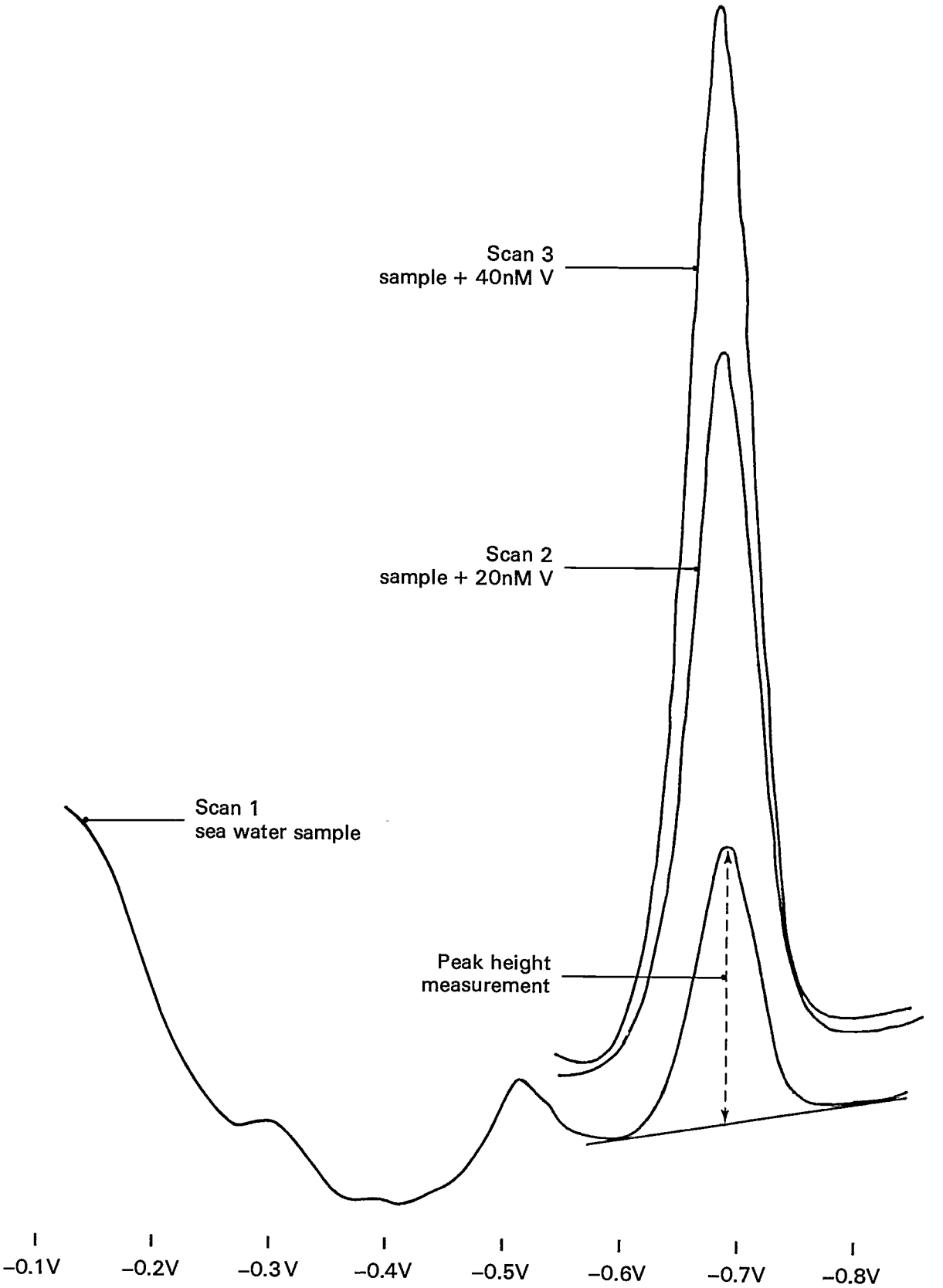


Figure 10 Calibration curve for the determination of vanadium

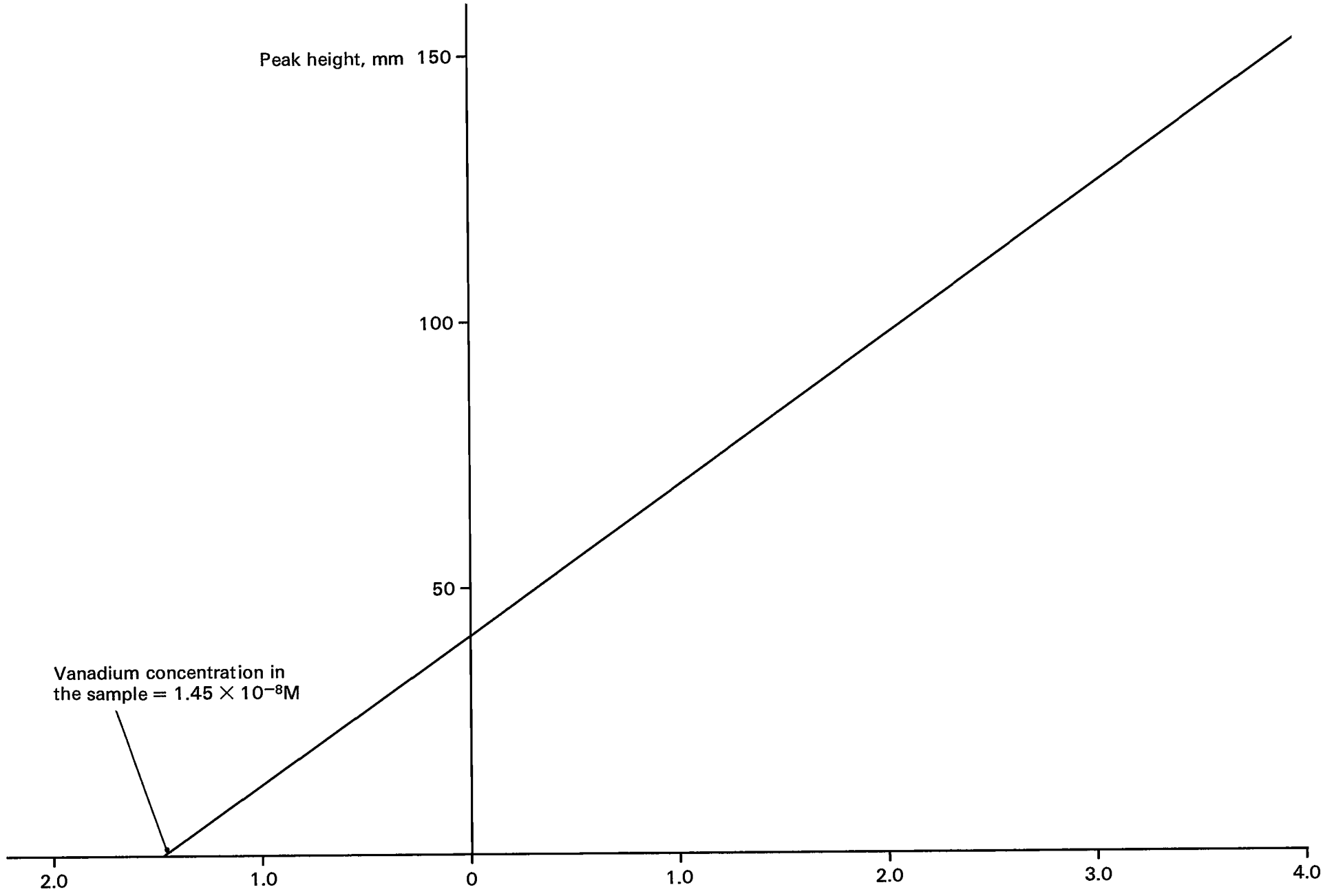
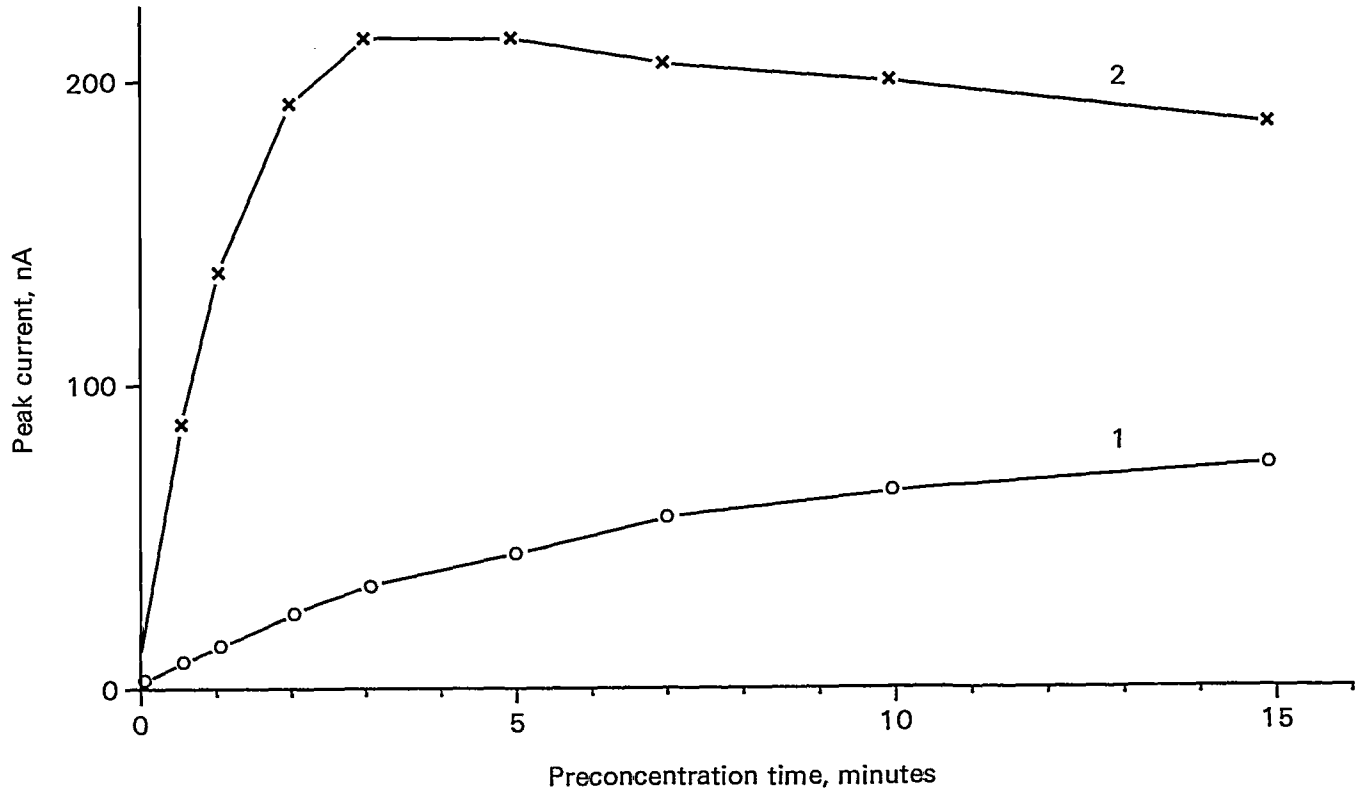


Figure 11 Effect of preconcentration time on the peak current



1 Vanadium concentration = 4.0×10^{-8}M

2 Vanadium concentration = 1.0×10^{-7}M

D Direct Determination of Dissolved Zinc in Fresh and Sea Waters by Differential Pulse Cathodic Stripping Voltammetry with the Hanging Mercury Drop Electrode

D1 Performance Characteristics of the method

D1.1 Substance determined

Dissolved zinc in 2^+ oxidation state

D1.2 Type of sample

Natural and sea waters.

D1.3 Basis of method

The electrodeposition of the complex formed between zinc (II) and APDC at the hanging mercury drop electrode (HMDE) surface, and its subsequent determination by differential pulse cathodic stripping voltammetry (DPCSV).

D1.4 Range of application (a)

Up to 2×10^{-7} M (13.1 μg 1^{-1}), (b).

D1.5 Calibration curve (a)

Linearity depends on adsorption time and stirring rate. It is linear up to 2.0×10^{-7} M (13.1 μg 1^{-1}) under the stated conditions (b).

D1.6 Standard deviation, (a)

	Zinc Concentration	Within Batch Standard Deviation	Degrees of Freedom
(i)	2.0×10^{-9} M (0.13 μgl^{-1})	4.7×10^{-11} M (3.1 ngl^{-1})	8
(ii)	3.1×10^{-8} M (2.0 μgl^{-1})	4.1×10^{-10} M (27 ngl^{-1})	6
(iii)	3.3×10^{-8} M (2.2 μgl^{-1})	5.6×10^{-10} M (37 ngl^{-1})	8
(iv)	3.6×10^{-8} M (2.4 μgl^{-1})	2.5×10^{-10} M (16 ngl^{-1})	8

(i) and (ii) Irradiated quartz distilled water
(iii) Irradiated coastal sea water
(iv) Irradiated river water

D1.7 Detection limit, (a)

1.4×10^{-10} M (9.2 ng 1^{-1}), (c).

D1.8 Sensitivity, (a)

(i) 1.5×10^{-8} MZn (0.98 μg 1^{-1}) gives a peak height of 15 nA
(ii) 1.5×10^{-8} MZn (0.98 μg^{-1}) gives a peak height of 13 nA
(i) UV irradiated sea water, adsorption time of 30 seconds.
(ii) UV irradiated quartz distilled water, adsorption time of 30 seconds.

D1.9 Bias

No bias was detected except when interferences occurred.

D1.10 Interferences

Certain substances cause interference in the determination of zinc (see Section D3).

D1.11 Time required for analysis

The typical time required for the analysis of one sample, is approximately 20 minutes; this excludes 2 hours for UV irradiation of the sample which is sometimes necessary to oxidize dissolved organic material; included are 8 minutes for purging of the sample and approximately 12 minutes for adsorption and scanning (when a 1 minute adsorption time is used) of the sample and two standard additions. The time varies, however, according to the sample volume used because larger sample volumes require longer purging times.

(a) Work carried out at the Department of Oceanography, University of Liverpool.

(b) Several factors can affect the linear response of this determination (see section D3.4).

(c) The detection limit can be reduced further by increasing the adsorption time.

D2 Principle

D2.1 The method is based upon the formation of APDC complexes of zinc (II) and their adsorption at the hanging mercury drop electrode (HMDE) at a controlled potential of -0.9 V vs a standard calomel reference electrode. The preconcentration is carried out over an accurately measured time period in a solution which is maintained at pH 7.3 by addition of BES buffer and which is stirred at a constant rate throughout. Preconcentration, by adsorption is followed by the analysis step in which the reduction current of the adsorbed complex of zinc is measured by differential pulse cathodic stripping voltammetry (DPCSV). The complex is reduced from the electrode using a linear potential ramp with pulses superimposed.

D2.2 Prior to analysis the sample is passed through a 0.45 μm membrane filter (see section D8) to remove particulate material, and is subsequently subjected to UV irradiation at a pH of 2.8 ± 0.2. UV irradiation is necessary to

(i) release zinc bound up with dissolved organic material, and

(ii) destroy both surface active and complex forming organic material which can cause interference (see section D3). Acidification is necessary to prevent loss of metal by adsorption onto the vessel walls during UV irradiation.

D2.3 The sample is brought to neutral pH by addition of ammonia. The BES buffer (D5.8) and complexing agent—APDC (D5.9), are added to an aliquot for analysis, the mixture is then purged with inert gas (Ar or N_2) in order to remove oxygen which is an interferent (see section D3). The sample is initially purged for 8 minutes (10 ml sample volume), or a longer period for larger sample volumes, and is thereafter purged for 60 s prior to subsequent measurements in the same sample solution.

D2.4 If all other conditions, (eg instrument settings, stirring rate pH etc) are kept constant, the sensitivity of the technique is directly dependent on the rate of deposition, which is in turn proportional to the diffusion rate of the complex ion onto the HMDE surface. The diffusion rate is temperature dependent and it is therefore necessary to ensure that the temperature is constant to within ± 0.5°C during a set of measurements (a 0.5°C change in temperature results in a variation in the rate of adsorption. and hence in the peak heights, of <1.5%). No special precautions need to be taken if the sample is at room temperature.

D2.5 Following the adsorption step, the stirrer is switched off and a period of 15 s is allowed to elapse, during which the solution comes to rest, before stripping is initiated.

D2.6 Following the 15 s waiting time, a potential ramp of 10 mVs^{-1} is applied, with pulses ($10\ s^{-1}$) superimposed on the ramp. Scanning using a current range appropriate to the expected zinc concentration the current is recorded and the output is obtained in the form of peaks, with heights proportional to the amount of electroactive species formed in the preconcentration step. At pH 7.3 the zinc peak is at a potential of about -1.16 V vs a SCE.

D2.7 The concentration of zinc in the sample is determined by the method of standard additions.

D3 Interferences

D3.1 Oxygen, surface active organic material, strong chelating compounds and some dissolved metals cause interference. The potential of the oxygen wave is very close to that of the zinc potential. It is important therefore that the sample is completely purged with an inert gas (Ar, or N_2) both prior to analysis, and in between analytical steps.

D3.2 Surface active organic material reduces the peak current for Zn considerably. The non-ionic surfactant Triton-X-100 has been previously used as a model for surface active organic material in sea water (41), and it was found that suppression of capacitance on a HMDE by surface active organic material in sea water was similar to that caused by 0.01–0.05 mg l^{-1} of Triton-X-100. The effect on the zinc peak of additions of Triton-X-100 to UV irradiated sea water is shown in table 6. UV irradiation of a sample at pH 2.8 ± 0.2 is sufficient to destroy surface active organic interferents.

D3.3 High concentration of strong chelating compounds can mask the Zn peak. The effect of additions of the chelating agent, EDTA, to irradiated sea water is shown in table 7. Natural organic complexing ligands, however, are much weaker complexes than EDTA, and are normally present in natural waters at lower concentrations than 10^{-5} M. UV irradiation is sufficient to destroy chelating interferents.

D3.4 Other metal ions can interfere in the determination of zinc if their complexes with APDC are adsorbed on the HMDE and their reduction peaks are close to that of Zn. At concentrations of 10^{-7} M Cu, Fe, V, U and Pb do not interfere. APDC, itself, produces a wave between −0.3 V and −0.8 V which masks any peaks produced by these elements. However, Ni (II) and Co (II) do produce peaks close to that of zinc and are potential interferents when present at relatively high concentrations. To avoid interference from high concentrations of Ni and Co, Zn can be determined selectively by using an alternative preconcentration step in which preconcentration is carried out at an initial potential of −1.3 V (as opposed to −0.9 V). The scan is then initiated from −0.9 V and the height of the Zn reduction peak is considerably enhanced relative to those of Co and Ni, as a result of the irreversible reduction of Co and Ni. (For a typical analytical procedure see section 9.11).

D4 Hazards

D4.1 Mercury

Mercury is toxic by inhalation and its effects as a poison are cumulative. Great care should therefore be taken in its handling and storage; see A4.1.

D5 Reagents

D5.1 Redistilled Water

The redistilled water used in the preparation of reagents and for the rinsing of apparatus can best be obtained from a double silica still. The organic content of this water is generally less than that produced by deionizers.

D5.2 50% (v/v) Hydrochloric Acid

Dilute 10 ml of ultrapure, 11.4 N hydrochloric acid to 20 ml by addition of redistilled water. It should be prepared freshly weekly, and stored in a polyethylene container.

D5.3 0.1 N Hydrochloric Acid

Dilute 4.4 ml of ultrapure, 11.4 N hydrochloric acid to 500 ml by addition of redistilled water. Store in a polyethylene container and use in the preparation of working standard solutions.

D5.4 1 N Nitric or Hydrochloric Acid

A reagent grade nitric or hydrochloric acid should be diluted with distilled water. Use the solution as an acid wash for soaking the cell, magnetic stirrer, glass pipettes and other glass and plastic ware.

D5.5 Standard Zinc Solution

D5.5.1 15.3×10^{-3} M Zn Standard (1,000 ppm), in 1 N HCl

Dissolve 1.000 ± 0.002 g of metallic zinc in 175 ml of 50% (v/v) HCl, transfer the solution to a 1 l calibrated flask and dilute to the mark with redistilled water. Store the solution in a clean polyethylene container. Alternatively, commercial standard solutions for atomic absorption spectrophotometry can be used.

D5.5.2 Suitable Working Standard Solutions are prepared from the above solution by dilution with 0.1 N HCl and are stored in clean polyethylene containers for up to 6 days.

D5.6 Mercury

Triple distilled mercury is used to fill the reservoir of the working electrode. This reagent is hazardous (see section D4).

D5.7 Saturated Potassium Chloride Solution

Shake 25 g of high purity KCl with 45 ± 1 ml of redistilled water until equilibrium is obtained. Use this solution to fill the salt bridge of the calomel reference electrode.

D5.8 1 M (pH 7.3) BES Buffer Solution

Dissolve 4.265 ± 0.01 g high purity N, N[1]-Bis-(2-hydroxyethyl)-2-amino-ethane sulphonic acid in 20 ml 0.5 M ammonia solution. Adjust to pH 7.3 by cautious addition of 50% (v/v) hydrochloric acid. Store in a clean polyethylene container.

Note: This reagent may require treatment to remove Zn impurities. This is best achieved by shaking overnight with 5×10^{-4} M 'MnO_2' suspension (A5.9) and then filtering through a 0.45 μm membrane filer.

D5.9 0.1 M APDC Solution

Dissolve 1.643 ± 0.002 g of ammonium pyrrolidine dithiocarbamate in 100 ml of redistilled water. Trace metal ion impurities are removed by extraction with three 10 ml portions of 1,1,2—trichloro 1,2,2—trifluoro-ethane.

D5.10 50% (v/v) Ammonia Solution

Dilute 10 ml of ultrapure, 18 M ammonia solution to 20 ml by addition of redistilled water. It is prepared freshly weekly and is stored in a polyethylene container.

D5.11 0.5 M Ammonia Solution

Dilute 2.8 ml of ultrapure, 18 M ammonia solution to 100 ml by addition of redistilled water. Store in a polyethylene container and use in the preparation of the BES buffer solution.

D6 Equipment

D6.1 Cleanliness

Where possible, plastic and glassware should be reserved solely for low level Zn determination. Clean all glassware by standing it in 1 N nitric or hydrochloric acid when not in use, and before use wash it with redistilled water several times. Stand the platinum counter electrode, the magnetic stirrer bar and the PTFE bubbling tube in 1 N acid when not in use and before use rinse thoroughly with redistilled water. Stand the calomel reference electrode in 3 M KCl solution, which has been acidified to approximately 0.1 N with 50% (v/v) HCl, when not in use and rinse thoroughly with redistilled water prior to use. After the measurement of each sample, rinse the outside of the working electrode glass capillary tube with redistilled water and after use store it either dry and covered or in redistilled water.

D6.2 A Hanging Mercury Drop Electrode (HMDE)

D6.3 A suitable Polarographic Analyser.

D6.4 A good quality X-Y or Y-time Chart Recorder.

D6.5 A glass or PTFE Electrochemical Cell which is either readily incorporated as a part of the electrode assembly or has its own sealable polyethylene lid with apertures for working electrode, reference electrode, purge gas bubbling tube, platinum counter electrode and pH electrode (optional).

D6.6 Standard Calomel (reference) Electrode (SCE)

The reference electrode is filled with saturated KCl solution to a level such that when the SCE is immersed in the sample solution, the sample solution level is above the level of the KCl solution in the SCE (see figure 2); this is to prevent a net outflow of KCl solution which may contain significant concentrations of Zn, to the sample solution. To avoid this form of contamination a double-junction reference electrode is recommended. The outer sleeve is then filled with 0.1 M KCl or with the sample.

D6.7 Platinum Wire Counter Electrode

D6.8 PTFE Bubbling Tube connected, via a drechsel bottle containing redistilled water, via a regulator to a cylinder of inert gas (Ar or N_2).

D6.9 An electronically controlled Magnetic Stirrer.

D6.10 A PTFE-coated Magnetic Stirrer Bar.

D6.11 A polycarbonate Pressure Filtration Apparatus for use with 47 mm diameter membrane filters (the Sartorius apparatus has been found satisfactory).

D6.12 0.45 μm Membrane Filters

Prior to use the filters are soaked in 0.1 N hydrochloric acid for 2–4 hours to remove trace metal impurities and thoroughly washed with distilled water. Immediately before use the filters are again rinsed thoroughly with redistilled water.

D6.13 UV Irradiation Chamber fitted with 1 KW-mercury lamp with concentrically arranged fused silica tubes of 150 ml capacity. (see fig 28).

D6.14 An Adjustable Micropipette variable between 10 μl and 100 μl.

D6.15 A good quality pH Meter and Electrode.

D7 Sample Collection

For the collection of surface water samples use clean, acid-washed plastic containers; for sub-surface collections use all plastic sample apparatus and suspend it on plastic-coated suspension cable. Care should be taken to avoid the collection of samples close to a ship or close to the exhaust of an outboard motor. In collecting a river or estuarine sample care should be taken to avoid collecting a non-representative sample.

D8 Pretreatment and storage of samples

Immediately after collection pass the sample (>500 ml) through a 0.45 μm membrane filter (previously rinsed with 0.1 M hydrochloric acid and rinsed with distilled water) using a pressure of 0.3 bar. Acidify 100 ml of sample by addition of 100 ± 5 μl of 50% (v/v) HCl. Irradiate the acidified sample for 2–3 hours in a clean silica tube. Store the irradiated sample in a clean PTFE or fused silica container until analysed.

D9 Analytical Procedure

Read section D4 on hazards before starting this procedure

Step	Procedure
D9.1	Bring 100 ml of the acidified, irradiated sample to neutral pH (7.8 ± 0.4) by addition of 75 ± 5 μl of 50% (v/v) ammonia solution.
D9.2	Accurately pipette 10 ml of sample into the electrochemical cell.

Step	Procedure

D9.3 Using a micropipette, add 75 μl of 1 M BES buffer to the sample solution.

D9.4 Using a micropipette, add 75 μl of 0.1 M APDC solution to the sample.

D9.5 Place a clean stirrer bar in the cell and put the cell into position on the stand ensuring an airtight seal around the rim.

D9.6 Gently bubble an inert gas (N_2 or Ar) through the sample for 8 minutes (a longer purging time is necessary for larger sample volumes).

D9.7 Meanwhile set up the polarograph as follows:

Initial potential	-0.9 V
Modulation (pulse) amplitude	25 mV
Scan rate	10 mVs^{-1} ($-$ve direction)
Drop time	0.1 s
Operating mode	Differential pulse
Low pass filter	Off
Current range	0–0.5 μA. (a)

(a) note that lower current range settings than 0.5 μA generally result in increased noise and hence difficulties in measuring peak heights; higher current range settings should be used for higher expected Zn concentrations.

D9.8 Once purging of the sample is complete and the polarograph is set up adsorption may be commenced. First the magnetic stirrer and the potentiostat are switched on (b). Once the sample solution is in steady motion adsorption is commenced by extruding a fresh mercury drop (c) and the timer is started. After a fixed adsorption time the stirrer is switched off, and after a further 15 s waiting period, during which the chart recorder is activated, the scan is initiated using a current range corresponding to the expected Zn concentration and the peak is recorded.

(b) The optimum stirring rate, which gives maximum sensitivity without too much turbulence in the sample solution, must be determined experimentally as it will vary with the shape of the electrochemical cell etc

(c) The mercury drop used when obtaining the test data had a volume of 3.56×10^{-4} cm^3, a radius of 4.4×10^{-2} cm and a surface area of 2.4×10^{-2} cm_2. Drops of slightly different size would be acceptable provided all drops used during the analysis are identical in size and shape.

D9.9 An appropriate standard addition of Zn is then made to the sample with a micropipette and the solution purged with an inert gas for one minute. The previous mercury drop is discarded and a further drop is formed and discarded before the working drop is extruded. Repeat the measurement as described in section D9.8. The volume of each standard addition should be small, ie <25 ul so as not to significantly alter the volume of the sample.

D9.10 A further addition of Zn standard is made and section D9.9 repeated.

D9.11 When Ni and/or Co are present at high concentrations they may interfere in this determination (see section D3.4), however, this problem can be overcome by adopting the following procedure.

D9.11.1 Proceed through steps D9.1–D9.6 as usual.

D9.11.2 Set up the polarograph as in section D9.6.

D9.11.3 With the cell disconnected from the polarograph (ie cell off, activate the recorder and scan from -0.9 V to -1.3 V then using the polarograph's HOLD function hold at -1.3 V. This operation is performed while the sample is being purged.

D9.11.4 Once purging of the sample is complete, and the polarograph has been set up, plating may be commenced. First the magnetic stirrer and potentiostat are switched on. Once the sample solution is in steady motion, plating is commenced by extruding a fresh mercury drop and the timer is started. After a fixed plating time the stirrer is switched off, a period of 15 s is allowed to elapse and the potential is then returned to the initial potential (-0.9 V). A further period of 15 s is allowed to elapse, during which the recorder is

Step	Procedure
	activated, and the scan is initiated over a current range corresponding to the expected Zn concentration and the peak is recorded (see figure 12).
D9.11.5	Standard additions of Zn are made and steps D9.11.2–D9.11.4 are repeated.

D10 Measurement of Peak Heights

The peak heights of the samples and the sample plus standard additions of zinc are plotted against the concentrations of added zinc standard in the manner illustrated in figure 13. The concentration of zinc in the sample is then read on the negative portion of the concentration z-axis.

D11 Sources of Errors

The analytical procedure can be applied to samples ranging from ultra-pure water to sea water, but as with most determinations of trace substances, the major source of error is the introduction of contaminants. The ways in which general contamination is avoided vary from laboratory to laboratory, analysts must decide on the precautions appropriate to their requirement. The use of a laminar flow cabinet is recommended. See Section A12.

With zinc, atmospheric contamination is a particular problem, eg via face powders, or from rubber gloves. Therefore in the manipulation of samples, reagents and standards the use of a laminar flow clean bench is strongly recommended. A laminar flow clean bench should also be used to house the electrode assembly.

D11.1 Leakage of contaminants into solution

Contaminants can leak into the sample solution from cell components, eg glass cell walls, the platinum electrode, or from the solution in the salt bridge of the reference electrode. This form of contamination manifests itself as successive increases in peak height when a series of replicate preconcentrations and scans are carried out on the same solution; all other conditions, ie temperature, stirring rate, preconcentration time etc, being constant. This type of contamination can be best avoided by leaving the cell components to soak in acid both between samples and when they are not in use; use the reference cell in the manner described in Section D6.6.

D11.2 Contaminants associated with reagents and standards

The second form of contamination may arise from the reagents used; taking into account the high quality reagents that are available this is not likely to be a significant factor.

D11.3 Interfering substances

For interference errors, see Section D3.

D12 Effect of Variations in the Preconcentration (or adsorption) Time

Measurements of the reduction current as a function of the adsorption time, are shown in figure 14. At high Zn concentrations the peak current levels out and then falls as an increasing area of the drop becomes covered first with Zn-APDC complex ions and then with complex ions of other metals, when adsorption times are prolonged (45).

D13 Checking the Accuracy of Analytical Results

Once the method has been put into routine use the main factor which will affect the accuracy of results (apart from contamination) will be operator errors, eg pipetting, peak height measurement etc. The effect of this was assessed by the determination, on six successive days, of Zn in a filtered and UV irradiated sea water sample. The mean concentration and standard deviation are presented here:

Mean concentration:	2.75×10^{-9} M Zn
Standard deviation:	0.125×10^{-9} M Zn
% standard deviation:	4.5%

(Data obtained at the Department of Oceanography, University of Liverpool).

Table 6

Effect of Triton-X-100 (non-ionic surfactant) on zinc peak in irradiated sea water; conditions: 10^{-3} M APDC, 0.01 M BES, 10 mVs^{-1} scan rate, 10 pulses s^{-1}, 25 mV pulse amplitude.

Triton-X-100 concentration, mg l^{-1}	Effect on Zn peak as a percentage of original peak height
0.5	−40%
1.0	−90%

Table 7

Effect of EDTA on zinc peak in irradiated sea water, conditions: 10^{-1} M APDC, pH 7.3, 4×10^{-8} M Zn.

EDTA Concentration	Effect on Zn peak as a percentage of original peak height
1×10^{-6} M	0
1×10^{-5} M	−11
3×10^{-5} M	−45
7×10^{-5} M	−86

Figure 12 Differential pulse polarography of zinc

Conditions: irradiated sea water; pH 7.3; initial potential –0.9V; scan rate 10mV s^{-1}; 25mV pulse amplitude; 10 pulses s^{-1}; 1.0μA current range

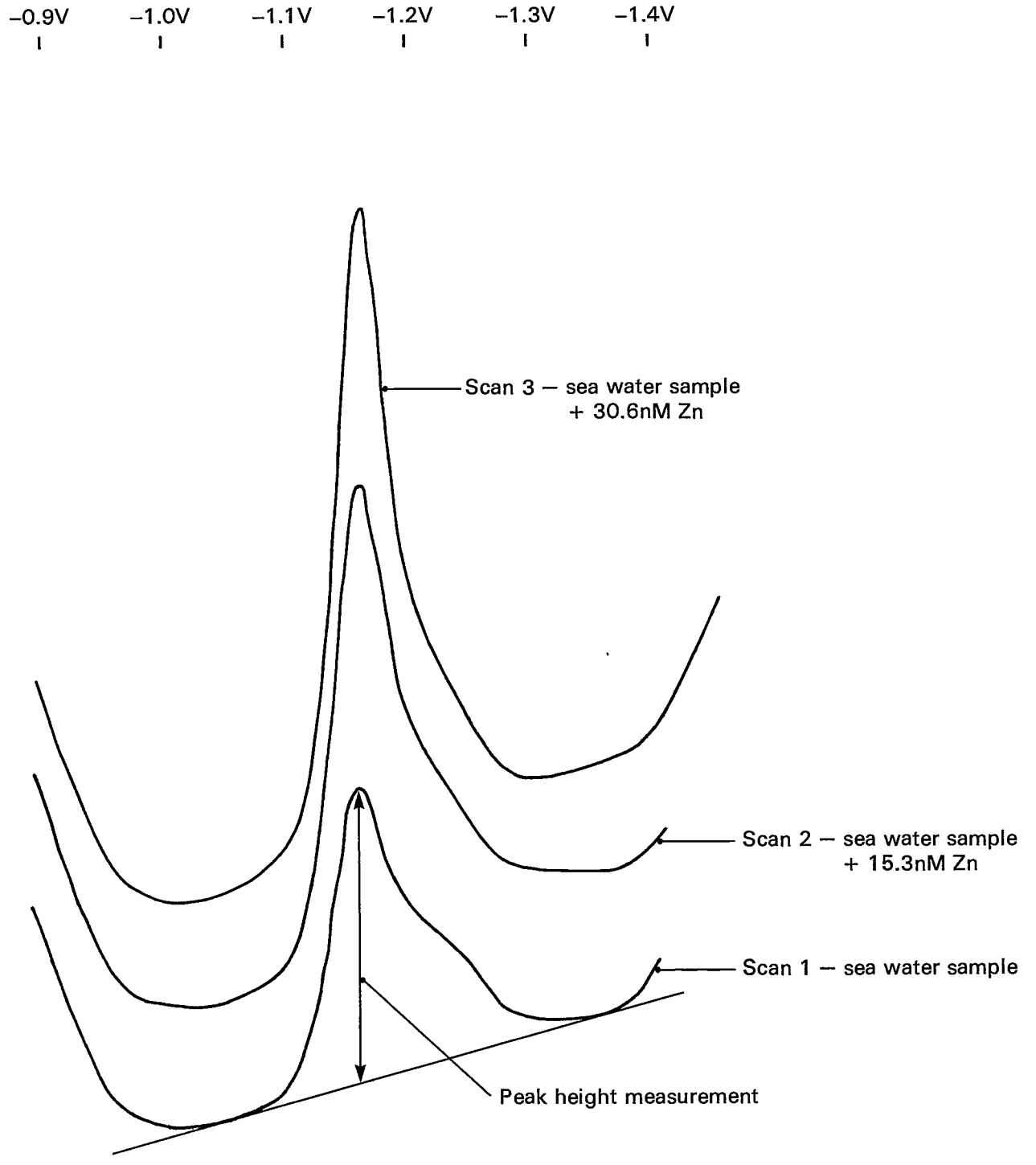


Figure 13 Calibration curve for the determination of Zn

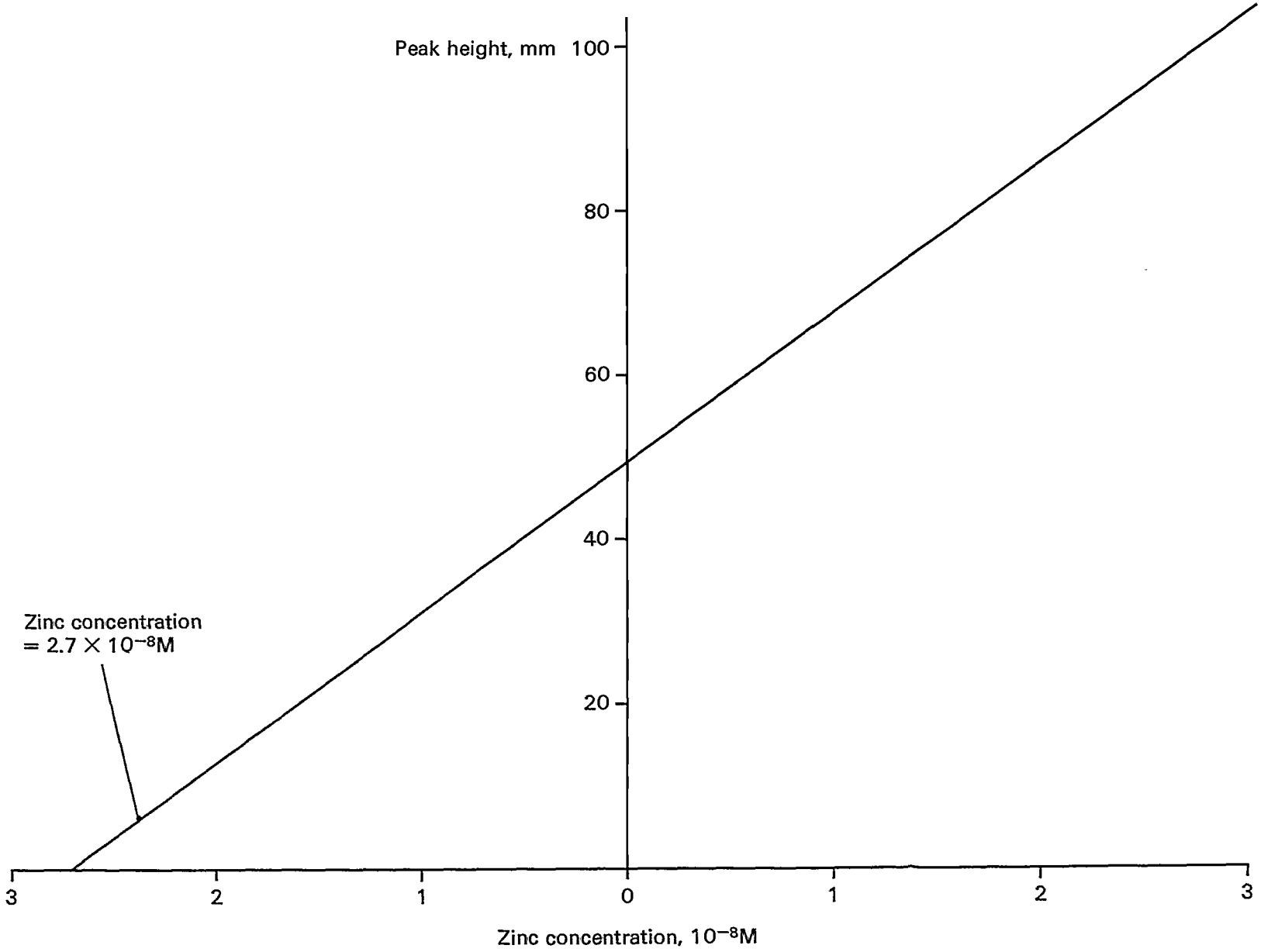
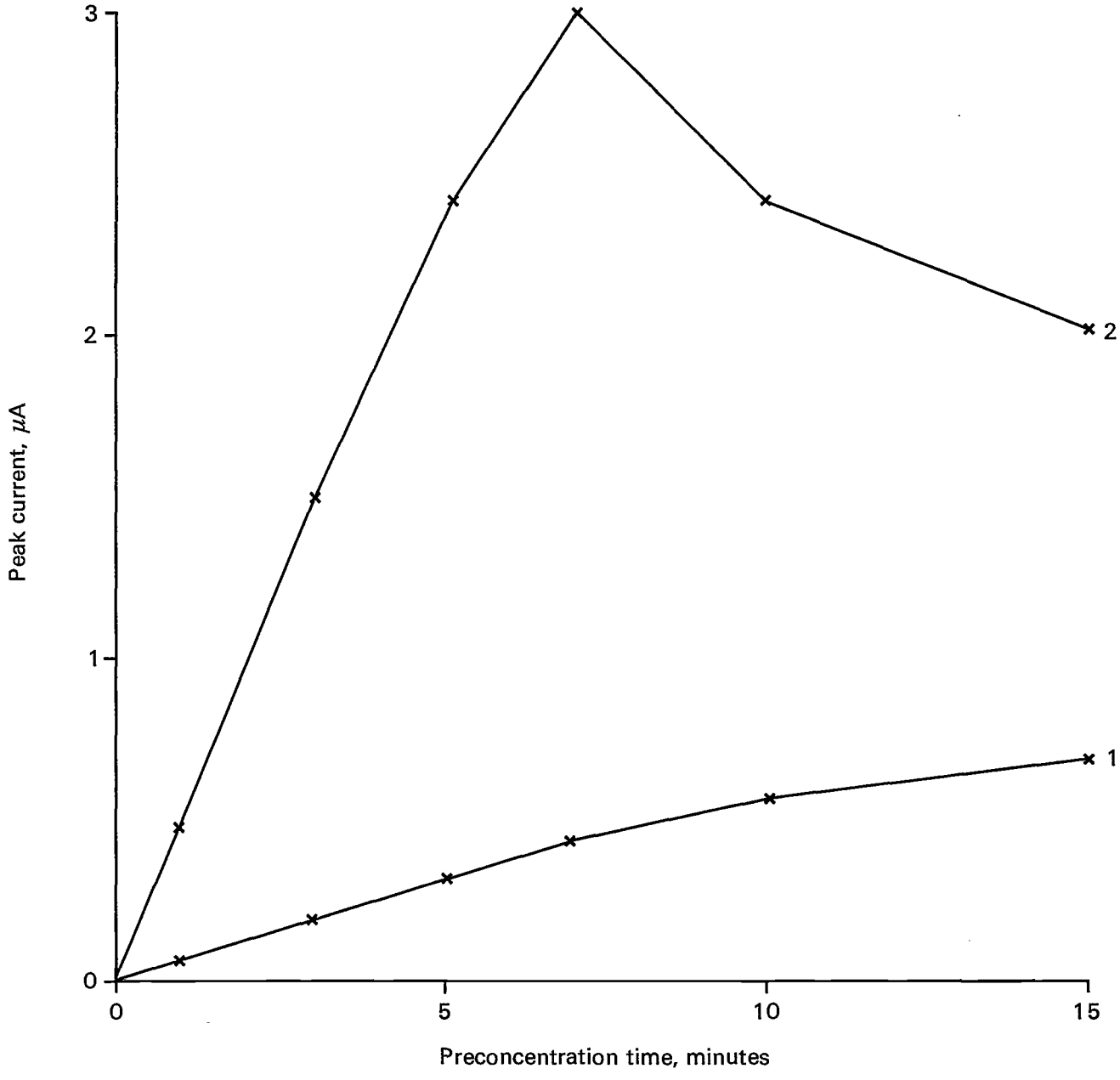


Figure 14 Effect of preconcentration time on peak current

Conditions: sea water (irradiated); pH 7.3; 10^{-3}M APDC; ALSV mode scan rate 50mV s^{-1}

1 Zn concentration = 3×10^{-8}M – linear to 7 minutes

2 Zn concentration = 2×10^{-7}M – linear to 3 minutes



E

Direct, Simultaneous Determination of Dissolved Nickel and Cobalt in Fresh and Sea Waters by Linear Sweep Cathodic Stripping Voltammetry with the Hanging Mercury Drop Electrode.

E1 Performance Characteristics of the Method.

(For an alternative chromopotentiometric method see Ref 68)

E1.1 Substance determined. Dissolved nickel (II) and cobalt (II).

E1.2 Type of sample. Sea water and other natural waters.

E1.3 Basis of the method. The electrodeposition of the complexes formed by nickel (II) and cobalt (II) with dimethylglyoxime (DMG), and their subsequent determination by linear sweep cathodic stripping voltammetry (LSCSV).

E1.4 Range of application (a).
Up to at least 10^{-6} M Ni and Co (58.7 and 58.9 ug l^{-1} respectively) (b).

E1.5 Calibration curve (a).
Linearity depends on adsorption time and stirring rate. It is linear with regard to both Ni and Co to at least 10^{-6} M (58.7 ug l^{-1}Ni and 58.9 ug l^{-1} Co) under the stated conditions (b).

E1.6 Total standard deviation (a).

	Nickel concentration	Within batch standard deviation	Degrees of freedom
(i)	7.2 nM (423 ng l^{-1})	1.3×10^{-10} M(7.6 ng l^{-1})	6
(ii)	25 nM (1.47 ug l^{-1})	4.4×10^{-10} M(25.8 ng l^{-1})	6
(iii)	1.8 nM (69.3 ng l^{-1})	0.4×10^{-10} M(2.3 ng l^{-1})	6
(iv)	18.3 nM (1.07 ug l^{-1})	2.7×10^{-10} M(15.8 ng l^{-1})	6
	Cobalt concentration	Within batch standard deviation	Degrees of freedom
(i)	2.5 nM (147 ng l^{-1})	5.5×10^{-11} M(3.2 ng l^{-1})	6
(ii)	16 nM (942 ng l^{-1})	2.0×10^{-10} M(11.8 ng l^{-1})	6
(iii)	1.48 nM (87 ng l^{-1})	0.3×10^{-10} M(1.8 ng l^{-1})	6
(iv)	6.92 nM (408 ng l^{-1})	0.9×10^{-10} M(5.3 ngl^{-1})	6

(i) Irradiated sea water.
(ii) Irradiated sea water spiked with Ni and Co.
(iii) Irradiated quartz distilled water.
(iv) Irradiated river water (from the River Test, Hampshire).

E1.7 Detection limit (a)

Ni: 1.3×10^{-10} M(7.6 ng l^{-1}) (c).
Co: 0.8×10^{-10} M(4.7 ng l^{-1}) (c).

E1.8 Sensitivity (a).
The sensitivity is dependent upon several variable factors including temperature, adsorption time and stirring rate. Under the stated conditions (d) the sensitivities of the technique to Ni and Co are:

Ni: 1 nM (58.7 ng l^{-1}) gives a peak current of 12.7 nA
Co: 1 nM (58.9 ng l^{-1}) gives a peak current of 13.8 nA

E1.9 Bias
No bias was detected except when interference occurred.

E1.10 Interferences.
Certain substances cause interference in the determination of Ni and Co (see section D3).

E1.11 Time required for analysis.

The typical time required for the analysis of one sample is approximately 15 minutes; this excludes 2 hours for UV irradiation of the sample which is sometimes necessary to oxidize dissolved organic material; included are 8 minutes for purging of the sample and approximately 7 minutes for adsorption and scanning (when a 1 minute adsorption time is used) of the sample and two standard additions. The time varies, however, according to the sample volume used because larger sample volumes required longer purging times.

(a) Work carried out at the Department of Oceanography, University of Liverpool.

(b) Several factors can affect the linear response of this determination. The greatest linear range is obtained when the solution is not stirred during the adsorption step. However, although it is possible to determine higher concentrations of Ni and Co than 10^{-6} M there is a danger of contaminating the electrode and cell components.

(c) Detection limits for a 1 minute adsorption time. Detection limits can be reduced further by increasing the adsorption time.

(d) Sensitivities for a 1 minute adsorption time and a stirred solution.

E2 Principle.

E2.1 The method is based upon the formation of DMG complexes of Ni (II) and Co (II) and their adsorption at the hanging mercury drop electrode (HMDE) at a controlled potential of -0.7 V vs a standard calomel reference electrode (SCE). The preconcentration is carried out for an accurately measured time in a solution which is maintained at a constant pH (8.3 for sea waters–9.0 for other natural waters) by addition of a boric acid/sodium hydroxide buffer and which is stirred at a constant rate throughout. Preconcentration, by adsorption, is followed by the analysis step in which the reduction currents of the adsorbed complexes of Ni (II) and Co (II) are measured by linear scan cathodic stripping voltammetry. In this case, the complex is reduced from the electrode using a linear potential ramp.

E2.2 Prior to analysis the sample is passed through a 0.45 um membrane filter (see section D8) to remove particulate material, and is subsequently subjected to UV irradiation at a pH of 2.8± 0.2. UV irradiation is necessary to

(i) release any nickel and cobalt which are bound up with organic material, and to

(ii) destroy both surface active and complex-forming organic material which can cause interferences (see section D3). Acidification is necessary to prevent loss of metal by adsorption onto the walls of the vessel during UV irradiation.

E2.3 The sample is brought to neutral pH by addition of ammonia solution, the boric acid/sodium hydroxide buffer and complexing agent, (DMG), are added to an aliquot for analysis, and the mixture is then purged with inert gas (Ar or N_2) in order to remove oxygen which is an interferent (see section D3). The sample (10 ml) is initially purged for 8 minutes or for a longer period for larger sample volumes, and is thereafter purged for 60 s prior to subsequent measurements in the same sample solution.

E2.4 If all other conditions, (eg instrument settings, stirring rate, pH etc.) are kept constant, the sensitivity of the technique is directly dependent on the rate of deposition which is in turn proportional to the rate of diffusion of the complex ions onto the HMDE surface. The diffusion rate is temperature dependent and it is therefore necessary to ensure that the temperature is constant to within ±0.5°C during a set of measurements (a 0.5°C change in temperature results in a variation in the rate of adsorption (and hence in the peak heights) of <1.5%). No special precautions need to be taken if the sample is at room temperature.

E2.5 Following the adsorption step, the stirrer is switched off and a period of 15 s is allowed to elapse, during which the solution comes to rest, before stripping is initiated.

E2.6 Following the 15 s waiting time, a potential ramp of 50 mVs^{-1} is applied. Scanning using a current range appropriate to the expected Ni and Co concentrations the current is recorded and the output is obtained in the form of peaks, with heights which are proportional to the amounts of electroactive species formed in the preconcentration step. At pH 8.3 (in irradiated sea water) the nickel and cobalt peaks are at potentials of about -1.01 V and about -1.13 V respectively. All peak potentials quoted are vs the SCE.

E2.7 The concentrations of Ni and Co in the sample are determined by the method of standard additions.

E2.8 In many natural waters the Co concentrations are considerably lower than those of Ni. There are several ways in which the sensitivity for Co of the technique can be enhanced. These include using a higher DMG concentration (8×10^{-4} M), an adsorption potention of -0.8 V, and longer adsorption times. Furthermore, the use of the differential pulse mode, as opposed to linear sweep, gives a larger cobalt peak, although it does not actually enhance the sensitivity in terms of peak current/Co concentration. (47).

E3 Interferences

E3.1 Oxygen, surface active organic material, strong chelating compounds and some dissolved metals cause interference. The potential of the oxygen wave is close to those of nickel and cobalt. It is important therefore that the sample is completely purged with an inert gas (Ar or N_2) both prior to analysis, and between analytical steps.

E3.2 Surface active organic material reduces the peak currents for Ni and Co considerably. The non-ionic surfactant Triton X–100 has been previously used as a model for surface active organic material in sea water (41), and it was found that suppression of capacitance on a HMDE by surface active organic material in sea water was similar to that caused by 0.01–0.05 mg l^{-1} of Triton X–100. The effect on the nickel and cobalt peaks of additions of Triton X–100 to irradiated sea water is shown in table 8. UV irradiation of a sample at pH 2.8± 0.2 is sufficient to destroy surface active organic interferents.

E3.3 High concentrations of strong chelating compounds can mask metal reduction peaks. Additions of the chelating agent, EDTA, to irradiated sea water had no effect on the Ni and Co reduction peaks in the presence of 4×10^{-4} M DMG, up to an EDTA concentration of 10^{-3} M. Natural organic complexing ligands, form much weaker complexes than EDTA, and are normally present in natural waters at lower concentrations than 10^{-5} M. They are unlikely, therefore, to interfere in the determination of Ni and Co and in any case are removed by UV irradiation.

E3.4 Some other metal ions can interfere in the determination of Ni and Co if their complexes with DMG are adsorbed on the HMDE and their reduction peaks are close to those of Ni and/or Co. The following metals at the stated concentrations were found to give no interference 10^{-9} M Se(VI), Ge, Tl(I); 4×10^{-9} M Sb(III); 10^{-8} M Pb, Cd Cr(VI), Ga,Se(IV), As(III), In; 2×10^{-8} M CrIII, Sn; 4×10^{-8} M Ti(III), AL; 10^{-7} M Zn, V(V), U(VI), Mo(VI); 2×10^{-7} M Cu, Fe(III), Mn(II) (conditions: 4×10^{-4} M DMG, 60 s adsorption time, 50 mVs^{-1} scan rate, UV irradiated sea water containing 10^{-8} M Ni and Co).

The reduction peaks of Ni and Co are separated by 0.14 V. Consequently high concentrations of one element may interfere in determination of low concentrations of the other. Up to a tenfold increase in Ni concentrations over that of Co caused no interference in Co determination and vice versa.

E4 Hazards

E4.1 Mercury

Mercury is toxic by inhalation and its effects as a poison are cumulative. Great care should therefore be taken in its handling and storage; see A4.1.

E5.1 Redistilled Water

The redistilled water used in the preparation of reagents and for the rinsing of apparatus can best be obtained from a double silica still. The organic content of this water is generally less than that produced by deionizers.

E5.2 50%(v/v) Hydrochloric Acid

Dilute 10 ml of ultra pure, 11.4 N hydrochloric acid to 20 ml by addition of redistilled water. It should be prepared freshly, weekly, and stored in a polyethylene container.

E5.3 0.1 N Hydrochloric Acid

Dilute 4.4 ml of ultra pure 11.4 N hydrochloric acid to 500 ml by addition of redistilled water. Store in a polythylene container and use in the preparation of working standard solutions.

E5.4 1 N Nitric or Hydrochloric Acid

Reagent grade nitric or hydrochloric acid should be diluted with distilled water. Use the solution as an acid wash for soaking the cell, magnetic stirrer, glass pipettes and other glass and plastic ware.

E5.5 Standard Nickel Solutions

E5.51 17.0×10^{-3} M Ni standard (1000 ppm), in 1 N HCl.

Dissolve 1.000±0.002 g of metallic nickel in 120 ml of 50% (v/v) nitric acid, transfer the solution to a 1 litre calibrated flask and dilute to the mark with redistilled water. Store the solution in a clean polyethylene container, alternatively, commercial standard solutions for atomic absorbtion spectrophotometry can be used.

E5.5.2 Suitable Working Nickel Standard Solutions are prepared from the above solution by dilution with 0.1 N hydrochloric acid and can be stored in a clean polyethylene container for up to six days.

E5.6 Standard Cobalt Solutions

E5.6.1 17.0×10^{-3} M Co Standard (1000 ppm), in 1 N HCl.

Dissolve 1.000±0.002 g of metallic cobalt in 175 ml of 50% (v/v) hydrochloric acid, transfer the solution to a 11 calibrated flask and dilute to the mark with redistilled water. Store the solution in a clean polyethylene container. Alternatively, commercial standard solutions for atomic absorption spectrophotometry can be used.

E5.6.2 Suitable Working Cobalt Standard Solutions are prepared from the above solution by dilution with 0.1 N hydrochloric acid and can be stored in clean polyethylene containers for up to six days.

E5.7 Mercury

Triple distilled mercury is used to fill the reservoir of the working electrode. This reagent is hazardous (see section 4).

E5.8 Saturated Potassium Chloride Solution

Shake 25 g of high purity KCl with 45±1 ml of redistilled water until equilibrium is obtained. Use this solution to fill the salt bridge of the calomel reference electrode.

E5.9 1 M Boric Acid Buffer Solution

Dissolve 6.18±0.01 g of analytical grade boric acid in 30 ml of 1 N sodium hydroxide solution. Transfer the solution to a 100 ml calibrated flask and dilute to the mark with redistilled water. Adjust to pH 8.3 – 8.4 by addition to 1 N sodium hydroxide solution. Store the solution in a clean polyethylene container and prepare afresh each week.

E5.10 0.1 M DMG Solution

Dissolve 0.116±0.001 g of analytical grade dimethylglyoxime in 3.5±0.1 ml of 1 N sodium hydroxide solution. Transfer to a 10 ml calibrated flask and dilute to volume with water. Store the solution in a clean polyethylene container and prepare freshly weekly.

E5.11 Sodium Hydroxide Solution

Dissolve 4.0 ± 0.1 g of analytical grade sodium hydroxide in 20 ml of redistilled water. Transfer the solution to a 100 ml calibrated flask and dilute to the mark with water. Store the solution in a clean polyethylene container.

E5.12 50% (v/v) Ammonia Solution

Dilute 10 ml of analytical grade ammonia solution to 20 ml by addition of redistilled water. Prepare afresh each weekly and store in a polyethylene container.

E6 Equipment

E6.1 Cleanliness

Where possible, plastic and glassware should be reserved solely for low level Ni and Co determinations. Clean all glassware by standing it in 1 N nitric or hydrochloric acid when not in use, and before use wash it with redistilled water several times. When not in use, stand the platinum counter electrode, the magnetic stirrer bar and the PTFE bubbling tube in 1 N acid, and stand the calomel reference electrode in 3 M KCl solution, which has been acidified to approximately 0.1 N with 50% (v/v) HCl; before use all these items rinse thoroughly with redistilled water. After the measurement of each sample rinse the outside of the working electrode glass capillary tube with redistilled water and after use store it either dry (covered) or in redistilled water.

E6.2 Hanging Mercury Drop Electrode (HMDE).

E6.3 A suitable Polarographic Analyser.

E6.4 A good quality X – Y or Y – time Chart Recorder.

E6.5 A glass or PTFE Electrochemical Cell which is either readily incorporated as a part of the electrode assembly or has its own sealable polyethylene lid with apertures for working electrode, reference electrode, purge gas bubbling tube, platinum counter electrode and pH electrode (optional).

E6.6 Standard Calomel (reference) Electrode (SCE)

The reference electrode is filled with saturated KCl solution to a level such that when the SCE is immersed in the sample solution, the sample solution level is above the level of the KCl solution in the SCE (see figure 2); this is to prevent a net outflow of KCl solution, which may contain significant concentrations of Ni and/or Co, to the sample solution. To avoid this form of contamination a double-junction reference electrode is recommended. The outer sleeve is then filled with 0.1 M KCl or with the sample.

E6.7 Platinum Wire Counter Electrode

E6.8 PTFE Bubbling Tube connected, via a drechsel bottle containing redistilled water, via a regulator to a cylinder of argon or oxygen-free nitrogen.

E6.9 An electronically controlled Magnetic Stirrer.

E6.10 A PTFE-coated Magnetic Stirrer Bar.

E6.11 A polycarbonate Pressure Filtration Apparatus for use with 47 mm diameter membrane filters (the Sartorius apparatus has been found satisfactory).

E6.12 0.45 μm Membrane Filters

Prior to use the filters are soaked in 0.1 N hydrochloric acid for 2–4 hours to remove trace metal impurities. Immediately before use the filters are rinsed thoroughly with redistilled water.

E6.13 UV Irradiation Chamber fitted with a 1 kW-mercury lamp with concentrically arranged fused silica tubes of 150 ml capacity. (see fig 28).

E6.14 An Adjustable Micropipette variable between 10 μl and 100 μl.

E6.15 A good quality pH Meter and Electrode.

E7 Sample Collection

For the collection of surface water samples use clean, acid-washed plastic containers; for sub-surface collections use all plastic sampling apparatus and suspend it on plastic-coated suspension cable. Care should be taken to avoid the collection of samples close to a ship or close to the exhaust of an outboard motor. In collecting a river or estuarine samples care should be taken to avoid collecting a non-representative sample.

E8 Pretreatment and Storage of Samples

Immediately after collection pass the sample (>500 ml) through a 0.45 μm membrane filter using a pressure of about 0.3 bar. Acidify 100 ml of sample by addition of 100 ± 5 μl of 50% (v/v) HCl. Irradiate the acidified sample for 2–3 hours in a clean silica tube. Store the irradiated sample in a clean PTFE or fused silica container until analysed.

E9 Analytical Procedure

Read section 4 on hazards before starting this procedure.

Step	Procedure

E9.1 Bring 100 ml of the acidified, irradiated sample to neutral pH (7.8 ± 0.4) by addition of 75 ± 5μl of 50% (v/v) ammonia solution.

E9.2 Accurately pipette 10 ml of sample into the electrochemical cell.

E9.3 Using a micropipette, add 100 μl of 1 M boric acid buffer to the sample solution.

E9.4 Using a micropipette, add 40 μl of 0.1 M DMG solution to the sample.

E9.5 Place a clean stirrer bar in the cell and put the cell into position on the stand ensuring an airtight seal around the rim.

E9.6 Gently bubble oxygen-free nitrogen or argon through the sample for 8 minutes (a longer purging time is necessary for large sample volumes).

E9.7 Set up the polarograph as follows:

Initial potential	−0.7 V
Scan rate	50 mVs^{-1}(−ve direction)
Drop time	off
Operating mode	Linear sweep (d.c)
Low pass filter	Off
Current range	0−0.2 μA. (a)

(a) note that lower current range settings than 0.2 μA generally result in increased noise and steeper base lines near to the hydrogen wave and hence cause difficulties in measuring peak heights; higher current range settings should be used for higher expected Ni and Co concentrations.

E9.8 Once purging of the sample is complete and the polarograph is set up, adsorption may be commenced. First, the magnetic stirrer and the potentiostat are switched on (b). Once the sample solution is in steady motion, adsorption is commenced by extruding a fresh mercury drop (c) and the timer is started. After a fixed adsorption time the stirrer is switched off, and after a further 15 s waiting period, during which the chart recorder is activated, the scan is initiated using a current range corresponding to the expected Ni and Co concentrations and the peak is recorded.

(b) the optimum stirring rate, which gives the maximum sensitivity without too much turbulence in the sample solution, must be determined experimentally as it will vary with the shape of the electrochemical cell etc.

(c) the mercury drop used when obtaining the test data had a volume of 3.56×10^{-4} cm^3, a radius of 4.4×10^{-2} cm and a surface area of 2.4×10^{-2} cm^2. Drops of slightly different size would be acceptable provided all drops used during the analysis are identical in size and shape.

Step	Procedure
E9.9	Appropriate standard additions of Ni and/or Co are then made to the sample which is then purged with an inert gas for one minute. The previous mercury drop is discarded and a further drop is formed and discarded before the working drop is extruded. Repeat the measurement as described in section 9.8. The volume of each standard addition should be small, ie <25 ul so as not to alter the volume of the sample significantly.
E9.10	Further additions of Ni and/or Co standard are made and section E9.9 is repeated. (see figure 15).

E.10. Measurements of Peak Heights

The peak heights for the sample and the sample plus standard additions of Ni and/or Co are plotted against the concentrations of added Ni and/or Co standard in the manner illustrated in figures 16 and 17. The concentrations of Ni and Co in the sample are then read on the negative extrapolation of the concentration axis.

E.11. Sources of Error

The analytical procedure can be applied to samples ranging from ultra-pure water to sea water, but as with most determination of trace substances, the major source of error is the introduction of contaminants. The ways in which general contamination is avoided vary from laboratory to laboratory, analysts must decide on the precautions appropriate to their requirements. The use of a laminar flow cabinet is recommended. See section A12.

Leave the cell components to soak in acid both in between samples and when they are not in use; use the reference cell in the manner described in Section D6.6.

For errors due to Interferences see Section E3.

E.12. Effect of Variations in the Preconcentration (or adsorption) Time

Measurements of the reduction current as a function of the adsorption time, are shown in figure 18. With long adsorption times the peak current probably levels out and then falls as an increasing proportion of the surface of the drop becomes covered first with Ni-DMG complex ions and then with complex ions of other metals (46). At higher initial Ni and Co concentrations of loss of linearity occurs at shorter adsorption times.

E13. Checking the Accuracy of Analytical Results

Once the method has been put into routine use the main factor which will affect the accuracy of results (apart from contamination) will be operator errors, eg pipetting, peak height measurement etc. The effect of these was assessed by the determination, on six successive days, of Ni and Co in a filtered and UV irradiated sea water sample. The mean concentration and standard deviation are presented here:

Mean concentration:	12.3×10^{-9} M Ni	4.01×10^{-9} M Co
Standard deviation:	0.45×10^{-9} M Ni	0.08×10^{-9} M Co
% standard deviation:	3.7%	2.0%

(Data obtained at the Department of Oceanography, University of Liverpool).

Table 8

Effect of Triton X–100 (non-ionic surfactant) on nickel and cobalt peaks in irradiated sea water; conditions: 4×10^{-4} N DMG, pH = 8.2 (boric acid/sodium hydroxide buffer), 50 mVs^{-1} scan rate, 60 s adsorption time.

Triton X–100 concentration, mgl^{-1}	Effect on peaks as a percentage of original peak heights	
	Ni	Co
0	0%	0%
0.1	−0.6%	0%
0.2	−1.0%	−0.6%
0.5	−12%	−17%
1.0	−100%	−100%

Figure 15 Linear sweep polarography of nickel and cobalt

Conditions : irradiated sea water; pH = 8.2; initial potential –0.7V scan rate 50mV s^{-1}; scan 1 current range 0 – 0.2μA; scans 2 and 3 current range 0 – 0.5μA

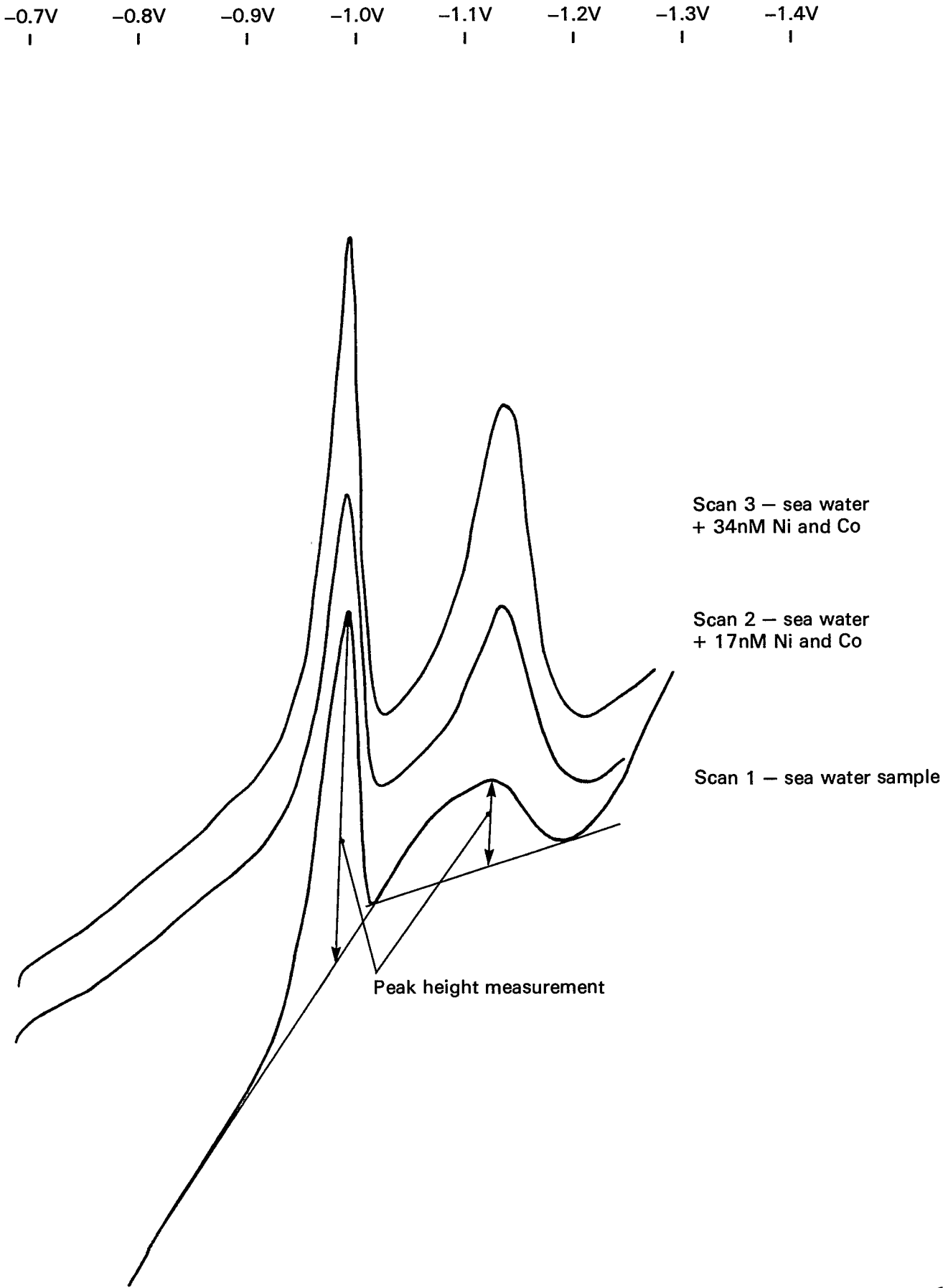


Figure 16 Calibration curve for the determination of nickel

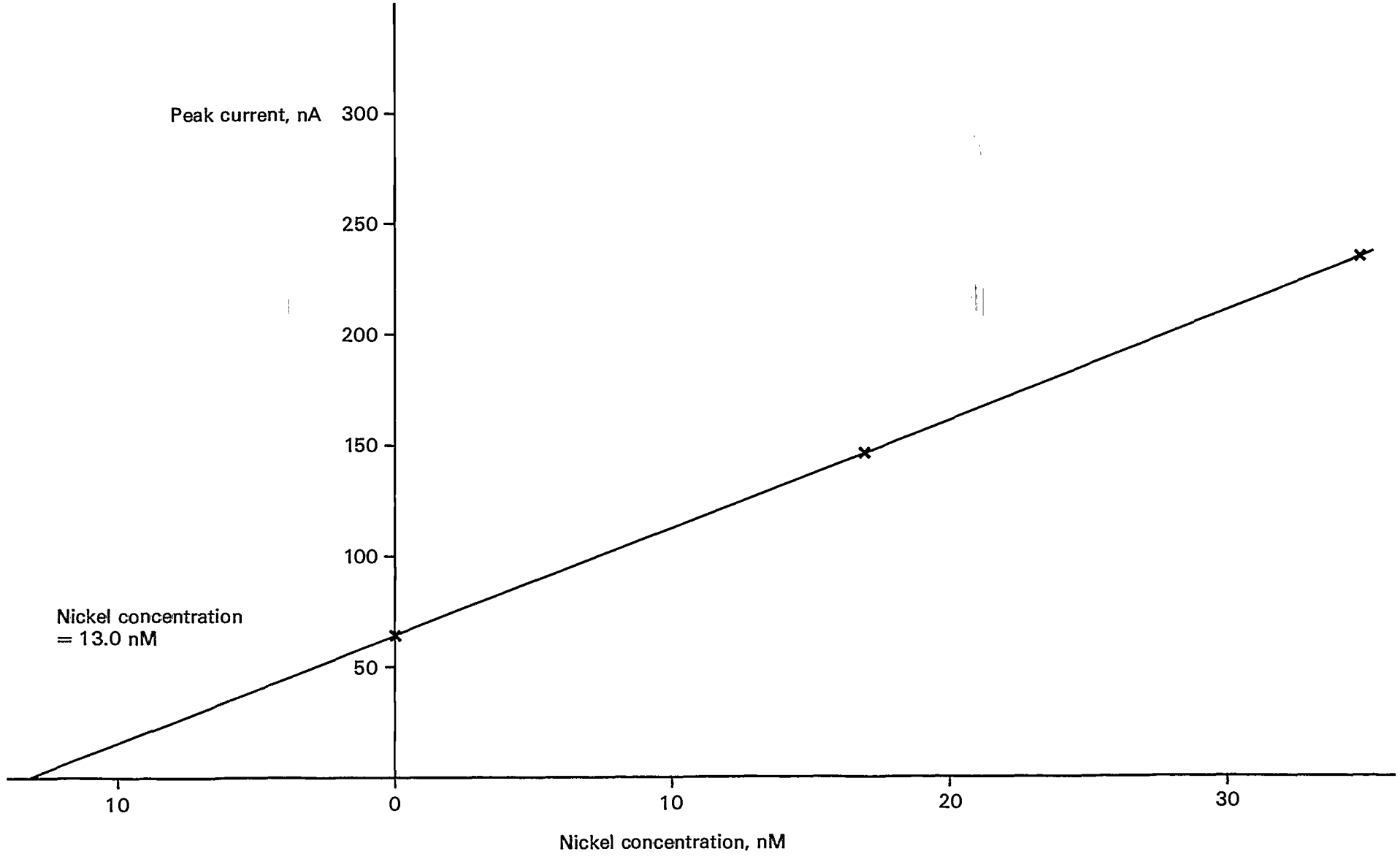


Figure 17 Calibration curve for the determination of cobalt

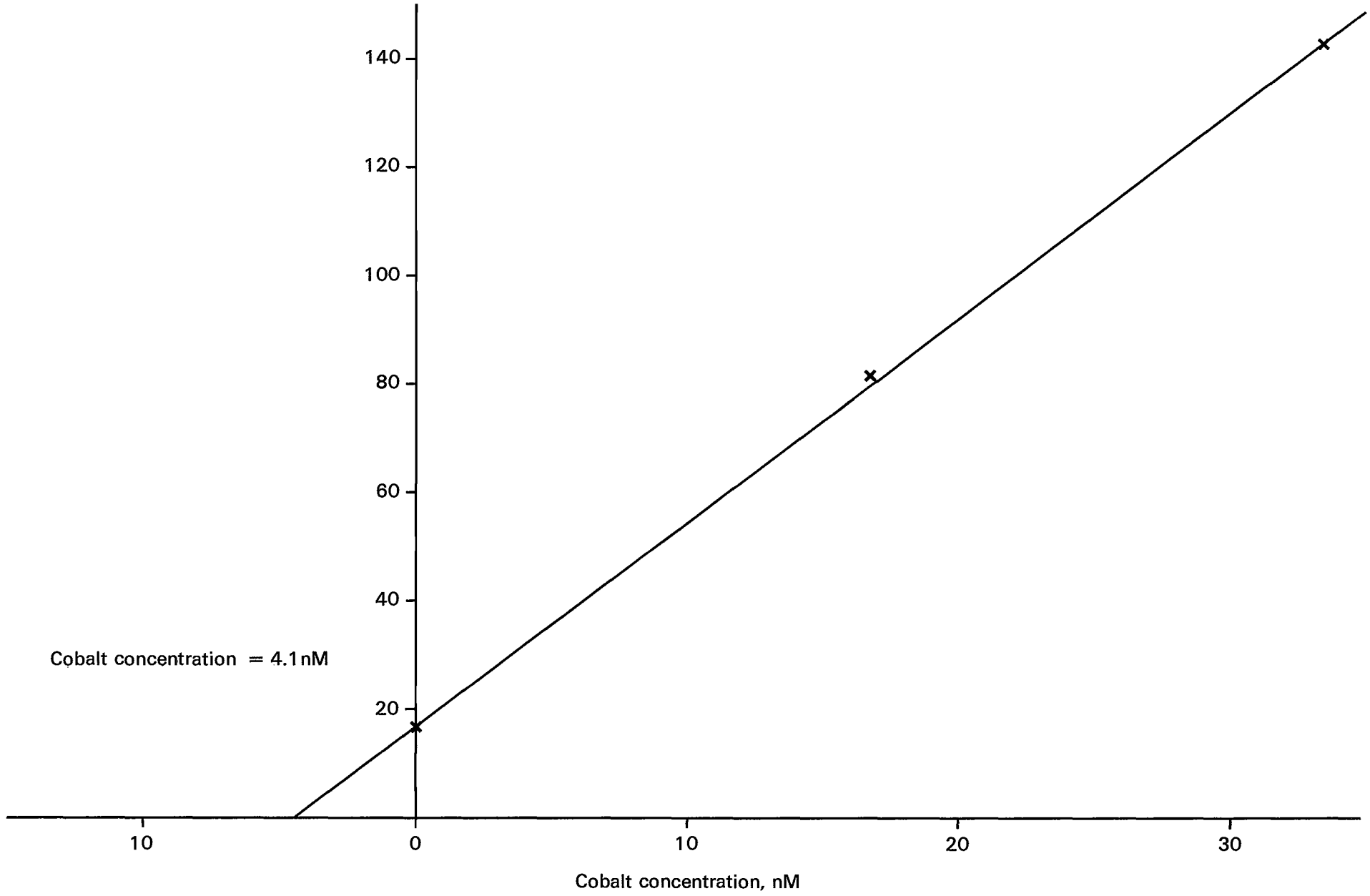
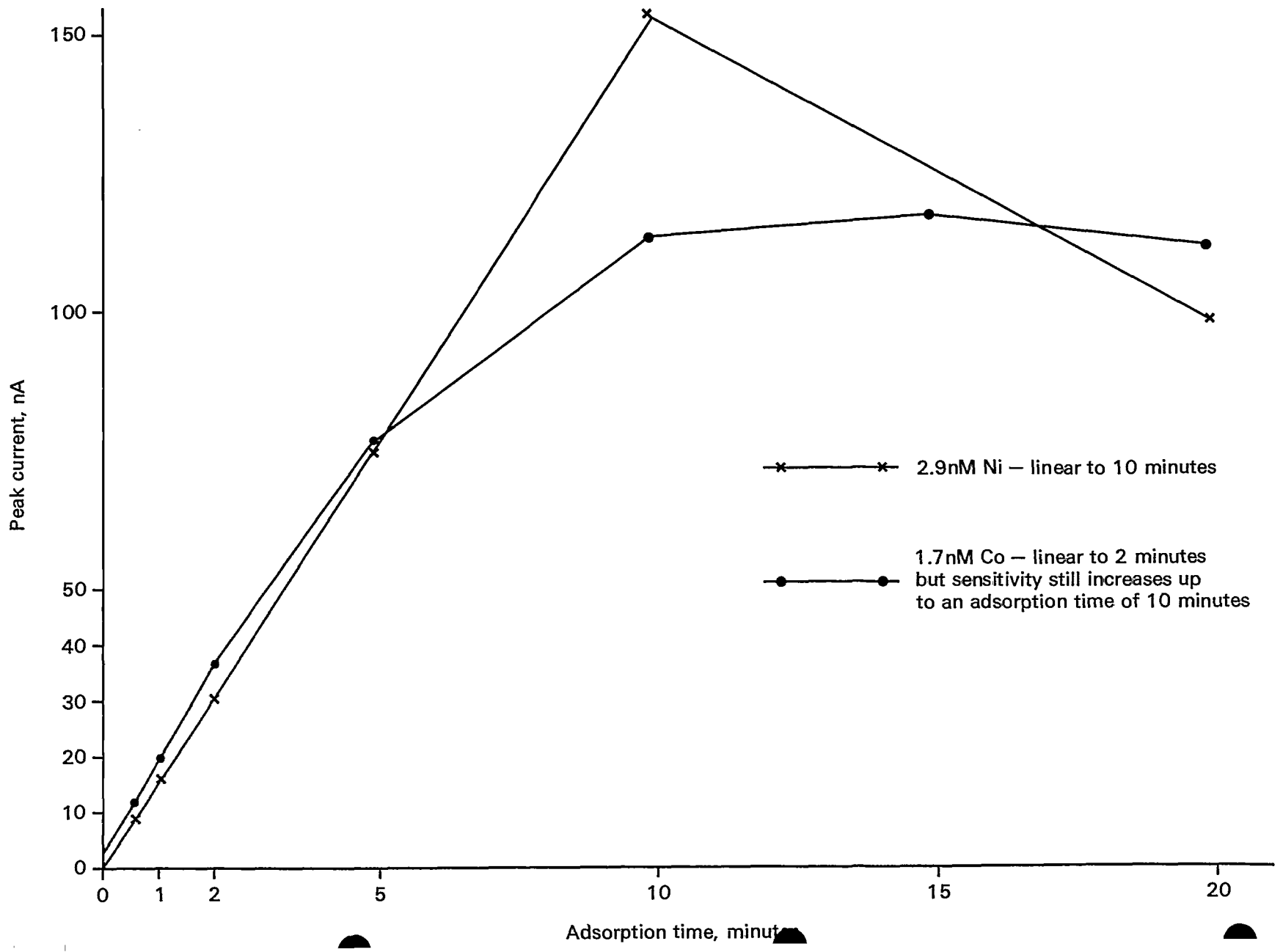


Figure 18 Effect of adsorption time on peak current

Conditions: irradiated quartz–distilled water; pH 9.0; 4×10^{-4}M DMG; 50mV s^{-1} scan rate



F Direct Determination of Uranium in Natural Waters by Linear Sweep Cathodic Stripping Voltammetry with the Hanging Mercury Drop Electrode.

F1 Performance Characteristics of the Method

(For an alternative Chromopotentiometric method see Ref 68)

F1.1 Substance determined.

Dissolved U in the 6^+ oxidation state.

F1.2 Type of sample

Sea water and other natural waters.

F1.3 Basis of method

The electrodeposition of the complex formed between uranium (VI) and 8–hydroxyquinoline (oxine) on the surface of a hanging mercury drop electrode (HMDE), and its subsequent determination by linear sweep cathodic stripping voltammetry.

F1.4 Range of application (a)

Up to 3×10^{-8} M (7.1 ug 1^{-1}) (b).

F1.5 Calibration curve (a)

Linearity depends on adsorption time and stirring rate. It is linear up to 3×10^{-8} M (7.1 ug 1^{-1}) under the stated conditions (b).

F1.6 Within Batch Standard deviation (a)

	Uranium	Concentration	Standard deviation	Degrees of freedom
(i)	0.5×10^{-9} M	(121 ngl^{-1})	0.5×10^{-10} M(12 ngl^{-1})	8
(ii)	22.0×10^{-9} M	(5.2 ugl^{-1})	0.7×10^{-9} M(167 ngl^{-1})	8

(i) Synthetic electrolyte solution.

(ii) Irradiated seawater spiked with U standard.

F1.7 Detection limit (a)

2.0×10^{-10} M (48 ngl^{-1}) (c).

F1.8 Sensitivity (a)

11 nM U gives a peak current of 3 nA after 1 minute preconcentration in sea water. Sensitivity is also dependent on stirring rate and can also be affected by interfering substances (see Section F3). Sensitivity is about 10% higher in fresh water.

F1.9 Bias

No bias was detected except when interference occurred.

F1.10 Interference

Certain substances cause interference in the determination of uranium (see section F3).

F1.11 Time required for analysis

The typical time required for the analysis of one sample is approximately 15 minutes; this includes 8 minutes for purging of the sample and approximately 7 minutes for adsorption and scanning of the sample and two standard

additions (when a 1 minute adsorption time is used). The time varies, however, according to the sample volume used because larger volumes require longer purging times.

Note: (a) Work carried out at the Department of Oceanography, University of Liverpool.

(b) Several factors can affect the linear response of the determination. The greatest linear range is obtained when the solution is not stirred during the adsorption step and short (eg 1 minute) adsorption times are used. However, although it is possible to determine higher concentrations of U than 10^{-7} M there is a danger of contaminating the electrode and cell components.

(c) Detection limit using a 1 minute adsorption time in a synthetic electrolyte solution. The detection limit can be reduced by increasing the adsorption time. For an adsorption time of 10 minutes the detection limit is 0.2×10^{-10} M.

F2 Principle

F2.1 The method is based upon the formation of oxine complexes of uranium (VI) and their adsorption at the hanging mercury drop electrode (HMDE) at a controlled potential of −0.4 V vs a standard calomel reference electrode. The preconcentration is carried out for an accurately measured time period in a solution which is maintained at pH 6.9 by addition of PIPES buffer and which is stirred at a constant rate. Preconcentration, by adsorption, is followed by the analysis step in which the reduction current of the adsorbed complex of U (VI) is measured by linear sweep cathodic stripping voltammetry. During this the complex is reduced from the electrode using a linear potential ramp with pulses superimposed.

F2.2 Prior to analysis, the sample is passed through a 0.45 μm membrane filter (see section F8) to remove particulate material, acidified to pH 2.6±0.2. and stored in either a quartz or a PTFE container.

F2.3 The sample is brought to neutral pH by addition of ammonia solution, the PIPES buffer is added to an aliquot for analysis and the mixture is then purged with inert gas (Ar or N_2) in order to remove oxygen which is an interferent (see section F3). The sample is initially purged for 8 minutes (10 ml sample volume), or for a longer period for larger sample volumes, and is thereafter purged for 60 s prior to subsequent measurements in the same sample solution.

F2.4 The complexing agent, oxine, is added and the sample is purged for a further 30 s.

F2.5 If all other conditions, (eg instrument settings, stirring rate, pH etc) are kept constant, the sensitivity of the technique is directly dependent on the rate of deposition which is in turn proportional to the rate of diffusion of the complex ions on to the HMDE surface. The diffusion rate is temperature dependent and it is therefore necessary to ensure that the temperature is constant to within ±0.5 °C during a set of measurements of (a 0.5 °C change in temperature results in variation in the rate of adsorption, and hence of the peak height of 1.5%). No special precautions need to be taken if the sample is at room temperature.

F2.6 Following the adsorption step, the stirrer is switched off and a period of 15 s is allowed to elapse, during which the solution comes to rest, before stripping is initiated.

F2.7 Following the 15 s waiting time, a potential ramp of 50m Vs^{-1} is applied. The current is recorded and the output is obtained in the form of peaks, with heights proportional to the amount of electroactive species formed in the preconcentration step. The uranium peak is at a potential of −0.68 V vs a SCE at a pH of 6.9.

F2.8 The concentration of uranium in the sample is determined by the method of standard additions.

F3 Interferences

F3.1 Oxygen, surface-active organic material, strong chelating compounds, carbonate and some dissolved metals cause interference. Oxygen, however, is removed by purging the sample with argon or nitrogen.

F3.2 Surface active organic materials reduce the peak current for U considerably. The non-ionic surfactant Triton-X-100 has been previously used as a model for surface active organic material in sea water (4), when it was found that suppression of capacitance on a HMDE by natural surface active organic materials in sea water was similar to that caused by 0.01–0.05 mgl^{-1} of Triton-X-100. The effect of additions of Triton-X-100 to sea water on the uranium peak current are shown in table 9.

F3.3 High concentrations of strong chelating compounds are known to mask some metal/complex reduction peaks. In sea water, at pH 6.9 with 2×10^{-5} M oxine and a U concentration of 1.4×10^{-8} N the uranium peak current is unaffected by EDTA concentrations up to 3×10^{-4} M but diminished by 25% when 10^{-3} M EDTA was added. Natural organic complexing ligands are much weaker complexing agents than EDTA and are present in natural waters at far lower concentrations than 10^{-3} M.

F3.4 Metals can interfere potentially in two ways:

(i) as a result of overlapping stripping peaks, and

(ii) as a result of competition other metal-oxine complexes for space on the HMDE surface.

F3.4.1 Overlapping stripping peaks arise when oxine complexes of other elements present in the sample have reduction potentials close to that of uranium. The uranium peak is at a potential of -0.68 V. Lead produces a small peak near to this at -0.59 V and Cd produces a peak at the same potential as U. However, both Cd and Pb are completely masked by adding 10^{-4} M EDTA to the sample. This has no effect on the sensitivity for U. Ni produces a peak at -1.02 V but is well separated from that of U. Zn produces a peak at -1.2 V, again well separated from that of U and is masked by 10^{-4} M EDTA. Additions of 10^{-7} M Fe(III), 5×10^{-8} M V, 2.5×10^{-8} M Mn, 5×10^{-8} M Al, 5×10^{-8} M Cr and 10^{-7} M Mo all failed to produce peaks. Sb(V) gives a peak at -0.83 V, well separated from that of U, but only at levels two orders of magnitude greater than those normally encountered in natural waters.

F3.4.2 Cu produces a peak at -0.47 V, well separated from that of U, but when high levels of Cu ($>2\times10^{-7}$ M) are present it can potentially interfere by partial saturation of the HMDE surface, thus diminishing the sensitivity towards U. This is overcome by selecting an adsorption potential which is nearer to and negative of the Cu peak, ie either at -0.45 or -0.50 V. Under these conditions the copper-oxine complexes dissociate as the copper is reduced; the copper then diffuses into the mercury drop.

F3.4.3 U(VI), as the uranyl ion UO_2^{2+}, is complexed by carbonate ions at neutral and high pH values. Thus the presence of carbonate ions is a source of interference in the determination of U in that they compete with oxine. This interference is conveniently removed by acidification of the sample to a pH of about 2.5, followed by purging with an inert gas (Ar or N_2). The sample is then returned to neutral pH by addition of NH_3 solution prior to the SCV determination itself.

F4 Hazards

F4.1 Mercury

Mercury is toxic by inhalation and its effects as a poison are cumulative. Great care should therefore be taken in its handling and storage; see A4.1.

F5 Reagents

F5.1 Redistilled Water

The redistilled water used in the preparation of reagents and for the rinsing of apparatus should be obtained from a double silica still. The organic content of this water is generally less than that produced by deionizers.

F5.2 50% (v/v) Hydrochloric Acid

Dilute 10±0.2 ml of ultrapure, 11.4 N hydrochloric acid to 20 ml by addition of redistilled water. It should be prepared freshly weekly and stored in a polyethylene container.

F5.3 0.1N Hydrochloric Acid

Dilute 4.4 ml of ultrapure, 11.4 N hydrochloric acid to 500 ml by addition of redistilled water. It should be stored in a polyethylene container and used in the preparation of working standard solution.

F5.4 1N Nitric or Hydrochloric Acid

Reagent grade nitric or hydrochloric acid should be diluted with distilled water and used as an acid wash for soaking the cell, magnetic stirrer, glass pipettes and other glass and plastic ware.

F5.5 Standard Uranium Solutions

F5.5.1 5×10^{-3} M U standard (1190 ppm), in 1NHCl. Dissolve 4.211±0.002 g of high purity uranium oxide, U_3O_8, in 175±3 ml of 50% (v/v) hydrochloric acid. Allow to dissolve , with agitation overnight. Transfer the solution to a 1 l calibrated flask and dilute to the mark with redistilled water. Store the solution in a clean polyethylene container.

F5.5.2 Suitable Working Standard Solutions are prepared from the above solution by dilution with 0.1 N HCl and are stored in clean polyethylene containers for up to 6 days.

F5.6 Mercury

Triple distilled mercury is used to fill the reservoir of the working electrode. This reagent is hazardous (see section F4).

F5.7 Saturated Potassium Chloride Solution

Shake 25 g of high purity KCl with 45±1 ml of redistilled water until equilibrium is obtained. Use this solution to fill the salt bridge of the calomel reference electrode.

F5.8 1M (pH 6.8 PIPES Buffer Solutions)

Dissolve 6.49±0.01 g high purity piperazine-N, N-bis-2-ethane sulphonic acid monosodium salt in 20 ml of 0.5 M ammonia solution. Adjust to pH6.8±0.2 by cautious addition of 50% (v/v) hydrochloric acid. Store in a clean polyethylene container.

F5.9 0.01M 8-Hydroxyquinoline

Dissolve 0.145±0.002 g of high purity 8-hydroxyquinoline (oxine) in 20 ml of 0.025 M high purity hydrochloric acid in a 100 ml calibrated flask. Dilute to volume with water and transfer to a polyethylene bottle. This reagent is stable for at least 2 weeks if kept in the dark.

F5.10 50% (v/v) Ammonia Solution

Dilute 10.0±0.2 ml of ultrapure, 18 M ammonia solution to 20 ml by addition of redistilled water. Prepare afresh each week and store in a polyethylene container.

F5.11 0.5M Ammonia Solution

Dilute 2.8±0.1 ml of ultrapure, 18 M ammonia solution to 100 ml by addition of redistilled water. Store in a polyethylene container and use in the preparation of the PIPES buffer solution.

F6 Equipment

F6.1 Cleanliness

Uranium is not a common laboratory contaminant but, where possible, plastic and glassware should be reserved solely for low level U determinations. Clean all glassware by standing it in 1 N nitric or hydrochloric acid when not in use, and before use wash it with redistilled water several times. Stand the platinum counter electrode, the magnetic stirrer bar and the PTFE bubbling tube in 1 N acid when not in use and before

use rinse thoroughly with redistilled water. Stand the calomel reference electrode, when not in use, in 3MKCl solution, which has been acidified to approximately 0.1 N with 50% (v/v) HCl, and rinse thoroughly with redistilled water prior to use. After the measurement of each sample rinse the outside of the working electrode glass capillary tube with redistilled water and after use store it either dry (covered) or in redistilled water.

F6.2 A Hanging Mercury Drop Electrode (HMDE)

F6.3 A suitable Polargraphic Analyser

F6.4 A glass or PTFE electrochemical cell which is either readily incorporated as part of the electrode assembly or has its own sealable polyethylene lid with apertures for working electrode, reference electrode, purge gas bubbling tube, platinum counter electrode and pH electrode (optional).

F6.5 Standard Calomel (reference) Electrode (SCE)

The reference electrode is filled with saturated KCl solution to a level such that when the SCE is immersed in the sample solution, the sample solution level is above that of the KCl solution in the SCE (see figure 2); this is to prevent a net outflow of KCl solution, which may contain significant concentrations of U, to the sample solution. To avoid this form of contamination the use of a double-junction reference electrode is recommended. The outer sleeve is then filled with 0.1M KCl or with the sample.

F6.6 Platinum Wire Counter Electrode

F6.7 PTFE Bubbling Tube connected, via a drechsel bottle containing redistilled water, via a regulator to a cylinder of inert gas (Ar or N_2).

F6.8 An electronically controlled Magnetic Stirrer

F6.9 A PTFE-coated Magnetic Stirrer Bar

F6.10 A polycarbonate Pressure Filtration Apparatus for use with 47 mm diameter membrane filters (The Sartorius apparatus has been found satisfactory).

F6.11 An Adjustable Micropipette variable between 10 μl and 100 μl.

F6.12 A good quality pH Meter and Electrode

F7 Sample Collection

For the collection of surface water samples use clean, acid-washed plastic containers; for sub-surface collections use all-plastic sampling apparatus and suspend it on plastic-coated suspension cable. See also F3.4. Care should be taken to avoid the collection of samples close to a ship or close to the exhaust of an outboard motor. In collecting river or estuarine samples care should be taken to collect a representative sample.

F8 Pretreatment and Storage of Samples

Immediately after collection pass the sample (>500 ml) through a 0.45 um membrane filter (which has been washed by soaking in 0.1 N hydrochloric acid and rinsing in redistilled water) using a pressure of about 0.3 bar. If the sample is to be stored prior to analysis then acidify it to pH 2.6±0.2 by addition of 100±5 μl of 50%(v/v) hydrochloric acid to each 100 ml of sample. Store it in a clean PTFE or fused silica container (see section F3.4).

F9 Analytical Procedure

Read section F4 on hazards before starting this procedure.

Step	Procedure
F9.1	Bring 100 ml of the acidified sample to neutral pH (7.8±0.4) by addition of 75± 5 μl of 50% (v/v) ammonia solution.

Step	Procedure

F9.2 Accurately pipette 10 ml of sample into the electrochemical cell.

F9.3 Using a micropipette, add 100 μl of 1 M PIPES buffer to the sample solution.

F9.4 Place a clean stirrer bar in the cell and put the cell into position on the stand ensuring an airtight seal around the rim.

F9.5 Gently bubble an inert gas (N_2 or Ar) through the sample for 8 minutes (a longer purging time is necessary for larger sample volumes).

F9.6 Set up the polarograph as follows:

Initial potential	-0.4 V
Scan rate	50 mVs^{-1} ($-$ve direction)
Drop time	Off
Operating mode	d.c.
Low pass filter	Off
Current range	$0-2\mu$A. (a)

(a) note that lower current range settings than 0.2 μA generally result in increased noise and hence difficulties in measuring peak heights; higher current range settings should be used if higher U concentrations are expected.

F9.7 Using a micropipette, add 20 μl of 0.01 M oxine solution (F5.9) to the sample and purge for a further 30 s.

F9.8 Once purging of the sample is complete and the polarograph is set up, adsorption may be commenced. First the magnetic stirrer and the potentiostat are switched on (b). Once the sample solution is in steady motion adsorption is commenced by extruding a fresh mercury drop (c) and the timer is started. After a fixed adsorption time the stirrer is switched off, and after a further 15 s waiting period, during which the chart recorder is activated, the scan is initiated over a current range corresponding to the expected U concentration and the peak is recorded.

(b) The optimum stirring rate, which gives maximum sensitivity without too much turbulence in the sample solution, must be determined experimentally as it will vary with the shape of the electrochemical cell etc.

(c) The mercury drop used when obtaining the test data had a volume of 3.56×10^{-4} cm^3, a radius of 4.4×10^{-2} cm and a surface area of 2.4×10^{-2} cm^2. Drops of slightly different size would be acceptable provided all drops used during the analysis are identical in size and shape.

F9.9 An appropriate standard addition of U is then made to the sample with a micropipette and the solution purged with an inert gas for one minute. The volume of each standard addition should be small, ie <25 μl, so as not to significantly alter the volume of the sample. The previous mercury drop is discarded and a further drop is formed and discarded before the working drop is extruded. Repeat the measurement as described in section F9.8 (see figure 19).

F9.10 A further addition of U standard is made and section F9.9 repeated.

F9.11 Some adjustments to the above procedure may be necessary to combat interference effects (see Section F3).

F10 Measurement of Peak Heights

The peak heights for the sample and the sample plus standard additions of uranium are plotted against the concentrations of added uranium standard in the manner illustrated in figure 20. The concentration of uranium in the sample is then read from the negative portion of the concentration axis.

F11 Sources of Errors

The analytical procedure can be applied to samples ranging from ultra-pure water to sea water, but as with most determinations of trace substances, the major source of error is the introduction of contaminants. The ways in which general contamination is avoided vary from laboratory to laboratory, analysts must decide on the precautions appropriate to their requirements. The use of a laminar flow cabinet is recommended.

See Section A12. Leave the cell components to soak in acid when they are not in use; use the reference cell in the manner described in section F6.6.

F12 Effect of Preconcentration (or adsorption) Time

For the effect of Interfering substances see section F3.

Measurements of the reduction current as a function of the adsorption time, are shown in figure 21. At elevated uranium concentrations the peak current levels out as an increasing area of the drop becomes covered with complex ions of U and other metals when adsorption times are prolonged (48).

F13 Checking the Accuracy of Analytical Results

Once the method has been put into routine use the main factor which will affect the accuracy of results (apart from contamination) will be operator errors, eg pipetting, peak height measurement etc. The effect of this was assessed by the determination, on six successive days of Uranium in a filtered sea water sample. The mean concentration and standard deviation were:

Mean concentration: 13.7 nM U (3.3 $\mu g l^{-1}$)
Standard deviation: 0.7 nM U (167 $ng l^{-1}$)
% standard deviation: 5.1%

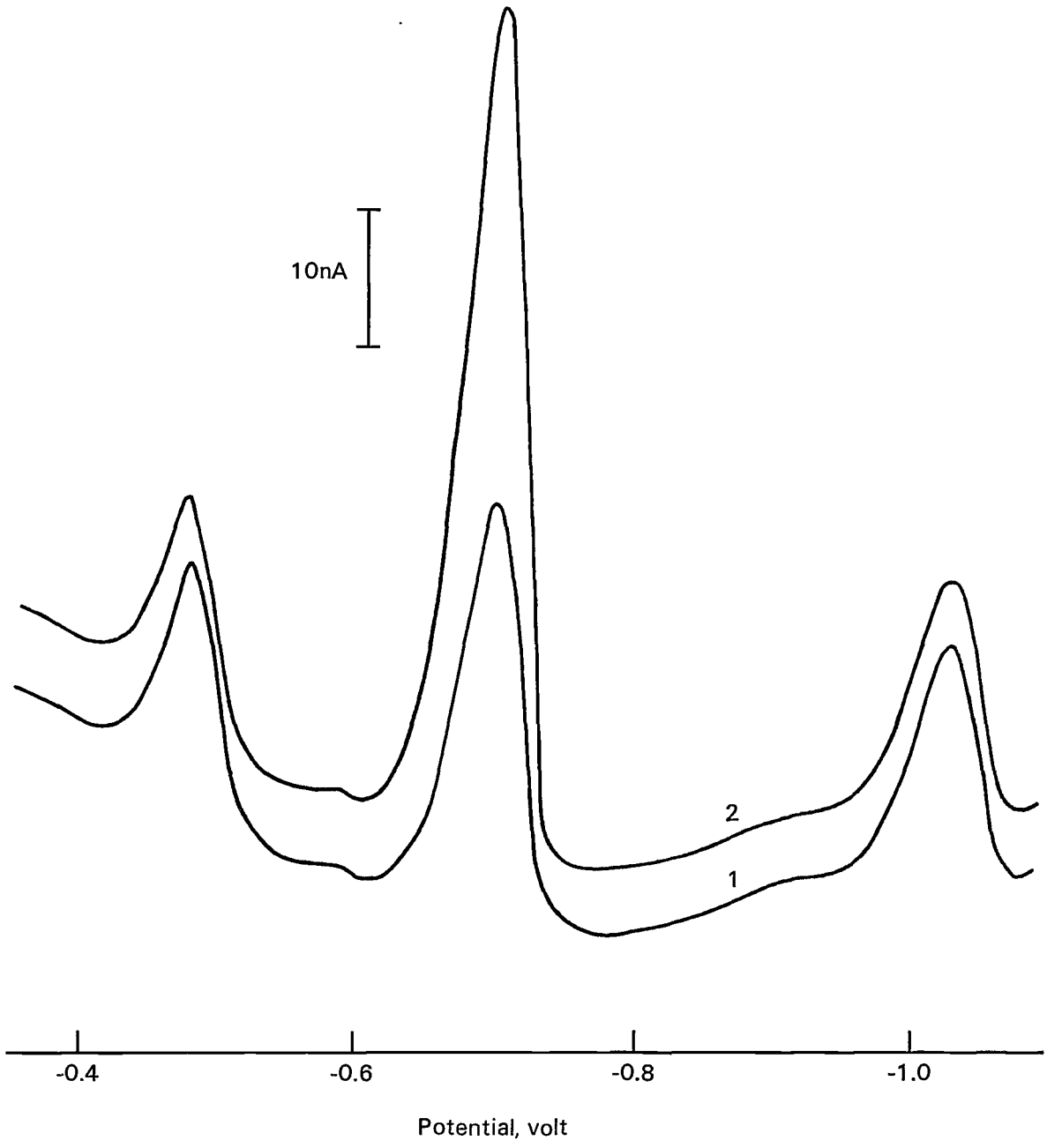
(Data obtained at the Department of Oceanography, University of Liverpool).

Table 9

Effect of Triton-X-100 (non-ionic surfactant) on the uranium peak in sea water; conditions: 1.4×10^{-8} M U, pH6.9, 1 minute adsorption time, 50 mVs^{-1} scan rate, initial potential −0.4 V, 25 mV pulse amplitude.

Triton-X-100 concentration, mg l^{-1}	Effect on U peak as a percentage of original peak height at an oxine concentration of:	
	5×10^{-5} M	5×10^{-4} M
0.1	−5%	
0.2	−10%	
0.5	−32%	
1.0	−42%	
2.0	−61%	
5.0	−69%	−12%

Figure 19 CSV of U in sea water



10^{-2}M PIPES (pH 6.9), $2x10^{-5}$M oxine, 1 minute adsorption at −0.35V

Scan 1: 9.5nM U

Scan 2: 10nM standard addition of U

Figure 20 Determination of U in sea water

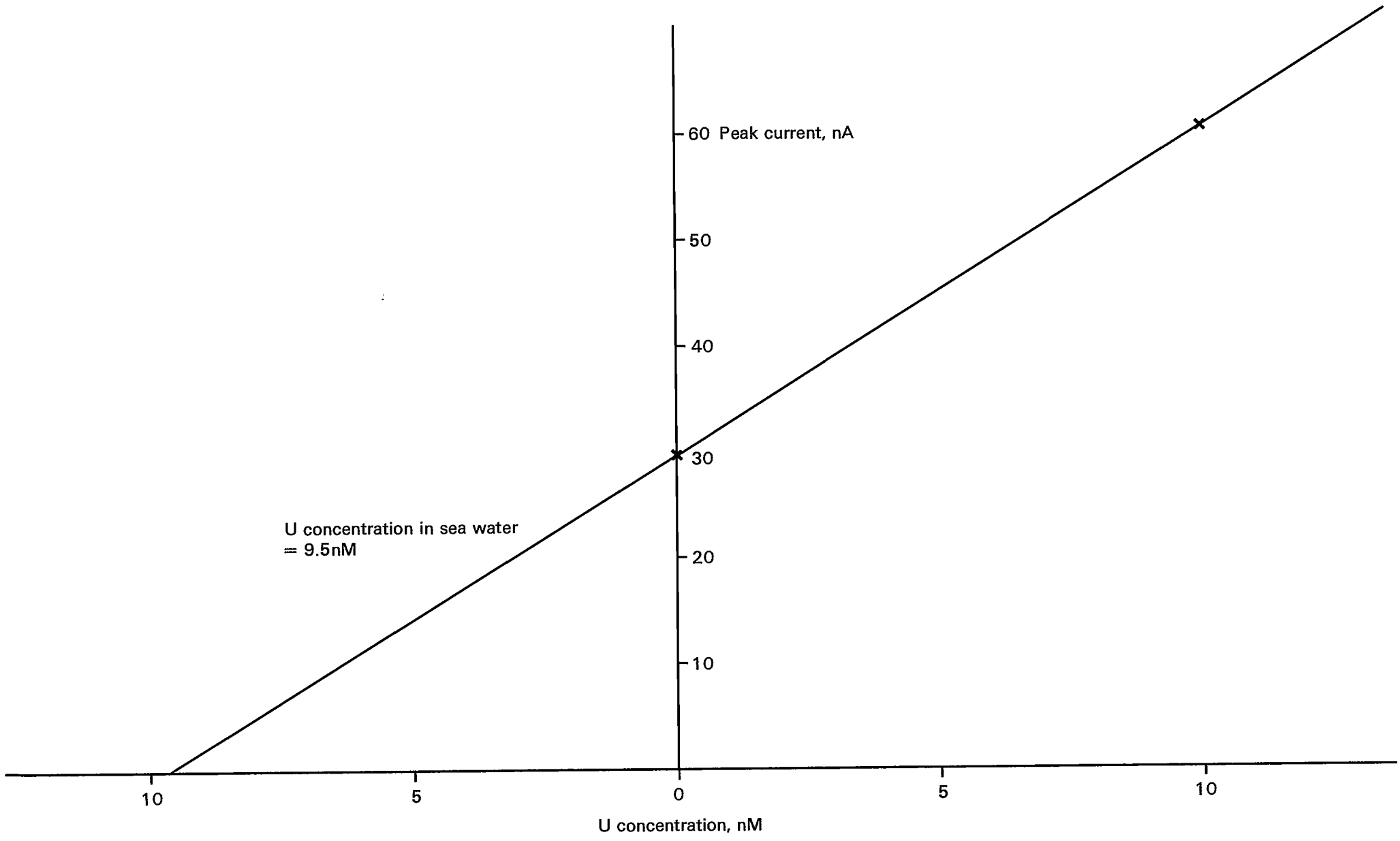
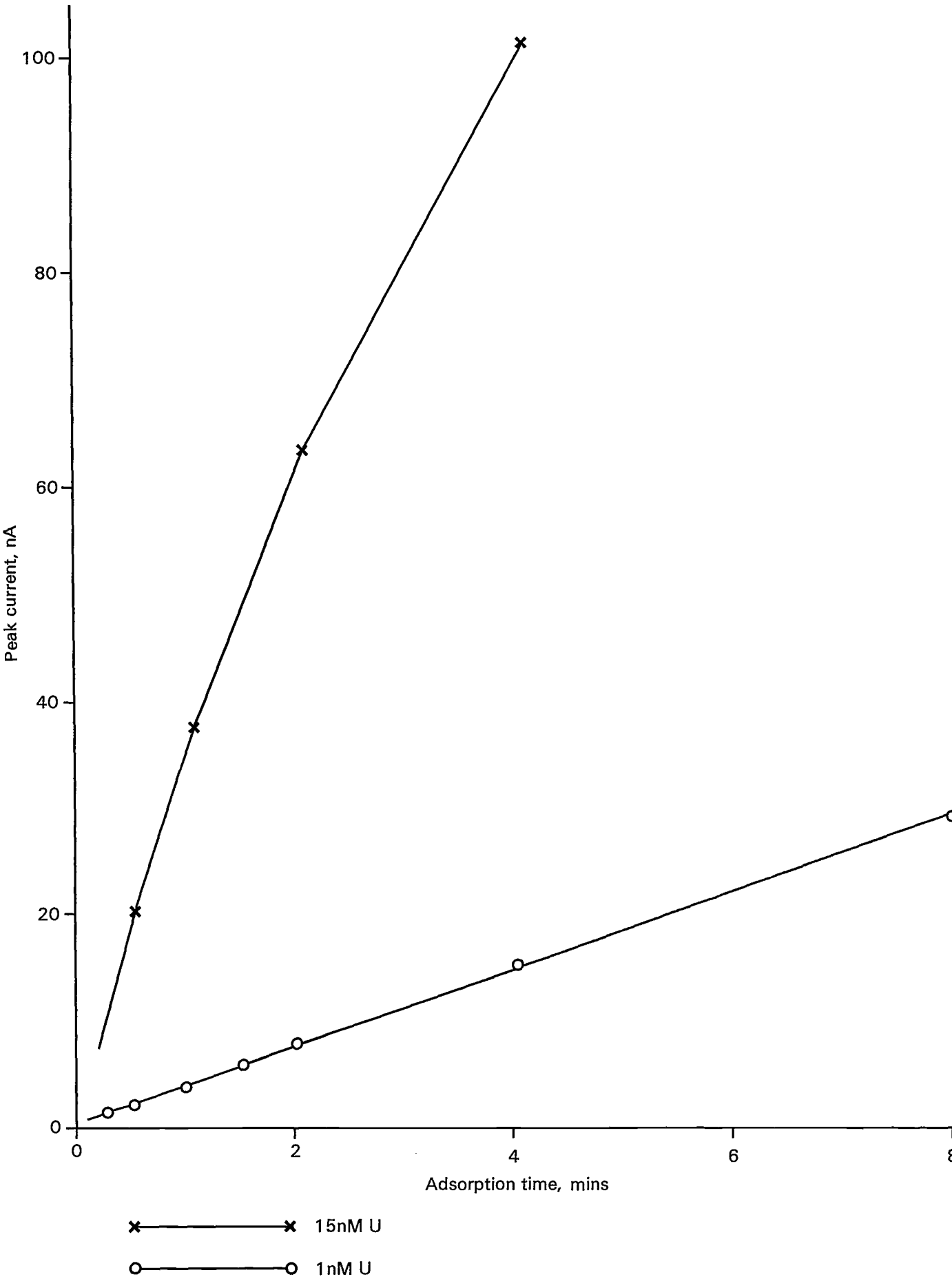


Figure 21 Effect of increasing adsorption time on the CSV peak current for U



Sea water, 10^{-2}M PIPES (pH 6.9)m 2 x 10^{-5}M oxine

G Direct Determination of Dissolved Aluminium in Fresh Sea Waters by Differential Pulse Cathodic Stripping Voltammetry with the Hanging Mercury Drop Electrode.

G1 Performance Characteristics of the Method

G1.1 Substances Determined.

Dissolved aluminium

G1.2 Type of sample

Sea waters, other natural waters and drinking water.

G1.3 Basis of the method

The electrodeposition of the complex formed between aluminium (III) and 1,2-dihydroxy anthraquinone-3 sulphonic acid, DASA, (Alizarin Red S) at the surface of the hanging mercury drop electrode (HMDE), and its subsequent determination by differential pulse cathodic stripping voltammetry (DPCSV). (49).

G1.4 Range of application, (a)

Up to 5×10^{-7} (13.5μg 1^{-1}), (b)

G1.5 Calibration curve, (a)
Linearity depends mainly on adsorption time and stirring rate. It is linear up to 5×10^{-1} M. Al (13.5±μg 1^{-1}) under the stated conditions (b).

G1.6 Total standard deviation, (a)

	Aluminium concentration	Within batch standard deviation	Degrees of freedom
(i)	15.4 nM (416ng1^{-1})	0.35 nM (9.5ng1^{-1})	8
(ii)	46.7 nM (1.26μg1^{-1})	0.9 nM 24.3ng1^{-1})	8
(iii)	46.8 nM (1.26μg1^{-1})	1.4 nM (38.9ng1^{-1})	8
(iv)	35.3 nM (953ng1^{-1})	0.6 nM (16.2ng1^{-1})	8
(v)	271 nM (7.3μg1^{-1})	3.0 nM (81ng1^{-1})	6

(i) Irradiated coastal sea waters.
(ii) Irradiated coastal sea water, spiked with Al standard.
(iii) Irradiated quartz distilled water.
(iv) Irradiated water from River Test.
(v) Irradiated tap waters.

G1.7 Detection limit, (a)

1.0 nM (27ng1^{-1})

G1.8 Sensitivity, (a)

(i) 7.4 nM Al (200ng1^{-1}) gives a peak current of 1.75nA.
(ii) 271 nM Al (7.3μg1^{-1}) gives a peak current of 7.3 nA.

(i) irradiated sea water, adsorption time 45 s, stirred sample.
(ii) irradiated tap water, adsorption time 30 s, unstirred sample.

G1.9 Bias

No bias was detected except when interference occurred.

G1.10 Interferences

Certain substances cause interference in the determination of aluminium (see section H3).

G1.11 The typical time required for the analysis of one 10 ml sample is approximately 20 minutes; this excludes two hours for UV irradiation of the sample which is sometimes necessary to destroy dissolved organic material; included are 8 minutes for purging of the sample and approximately 12 minutes for adsorption and scanning (when a 1 minute adsorption time is used) of the sample and two standard additions. The time required for analysis varies, however, according to the sample volume used, because larger sample volumes require longer purging times.

(a) Work carried out at the Department of Oceanography, University of Liverpool.

(b) Several factors can affect the linear response of this determination. Saturation of the drop with dissolved organic interferents can severely limit the linear range.

(c) The detection limit can be further reduced by increasing the adsorption time.

G2 Principle

G2.1 The method is based upon the formation of complex ions between aluminium (III) and 1,2-dihydroxyanthraquinone-3-sulphonic acid (DASA) and their subsequent adsorption at the hanging mercury drop electrode (HMDE) at a controlled potential of -0.9V (in sea water in absence of high Zn concentrations) vs a standard calomel reference electrode. The preconcentration is carried out over an accurately measured time period in a solution which is maintained at pH 7.1 by addition of a BES buffer and which is stirred at a constant rate throughout. Preconcentration, by adsorption, is followed by the analysis step in which the reduction current of the adsorbed ligand of aluminium is measured by differential pulse cathodic stripping voltammetry (DPCSV). The ligand is reduced from the electrode using a linear potential ramp with pulses superimposed.

G2.2 Prior to analysis the sample is passed through a 0.45μm membrane filter (see section G8) to remove particulate material, and is subsequently subjected to UV irradiation at pH of 2.80±0.2. UV irradiation is necessary to

(i) release aluminium bound up with dissolved organic material, and

(ii) destroy both surface active and complex forming organic material which can cause interference (see section H3). Acidification is necessary to prevent loss of metal by adsorption onto the vessel walls during UV irradiation.

G2.3 The sample is brought to neutral pH by addition of sodium hydroxide solution. The BES buffer and complexing agent, DASA, are added to an aliquot for analysis, the mixture is then purged with inert gas (Ar or N_2) in order to remove oxygen which is an interferent (see section G3). The sample is initially purged for 8 minutes (10 ml sample volume) and is therefore purged for 60 s prior to subsequent measurements in the same sample solution.

G2.4 If all other conditions, (eg instrument settings, stirring rate, pH etc) are kept constant, the sensitivity of the technique is directly dependent on the rate of deposition, which is in turn proportional to the diffusion rate of the complex ion onto the HMDE surface. The diffusion rate is temperature dependent and it is therefore necessary to ensure that the temperature is constant to within $+0.5$°C during a set of measurements (a 0.5°C change in temperature results in a variation in the rate of adsorption, and hence in peak heights, of 1.5%). No special precautions need to be taken if the sample is at room temperature.

G2.5 Following the adsorption step, the stirrer is switched off and a period of 15 s is allowed to elapse, during which the solution comes to rest, before stripping is inititated.

G2.6 Following the 15 s waiting time, a potential ramp of 20 mVs^{-1} is applied, with pulses (10 s^{-1}) superimposed on the ramp. Scanning, using a current range appropriate to the expected aluminium concentration, the current is recorded and the output is obtained in the form of peaks, with heights proportional to the amount of electroactive species formed in the preconcentration step. At pH 7.1 the aluminium peak is at a potential of about -1.13 V vs a SCE (in sea water) and about -1.06 V vs a SCE (in quartz-distilled water).

G2.7 The concentration of aluminium in the sample is determined by the method of standard additions.

G3 Interferences

Oxygen, surface active organic material, strong chelating compounds and some dissolved metals cause interference. Low pH can affect results.

G3.1 The potential of the oxygen wave is very close to that of the aluminium-DASA complex potential. It is important therefore that the sample is completely purged with an inert gas (Ar or N_2) both prior to the analysis and in between analytical steps.

G3.2 Surface active organic material reduces the peak current for aluminium considerably. The non-ionic surfactant Triton-X-100 has been previously used as a model for surface active organic material in sea water (41), and it was found that suppression of capacitance on a HMDE by surface active organic material in sea water was similar to that caused by 0.01–05 mgl^{-1} of Triton-X-100. The effect on the aluminium peak of additions of Triton-X-100 to UV irradiated sea water is shown in table 10. UV irradiation of sample at pH2.8±0.2 is sufficient to destroy surface active organic interferents.

G3.3 High concentrations of strong chelating compounds can mask metal peaks in electrochemical determinations. Additions of the chelating agent EDTA up to 10^{-4} M have no effect on the aluminium peak. However, the addition of EDTA did have the beneficial effect of masking the Zn peak which precedes that of Al (see section G3.4).

G3.4 Other metal ions can interfere in the determination of aluminium if their complexes with DASA are adsorbed on the HMDE and their reduction potentials are close to that of Al. The following metals at the stated concentrations do not interfere: 10^{-7} M Cu, Fe(III), Ni, As, In, Se(IV), V, Cr(III); 5×10^{-8} M Cd, Pb, Ti, Sn(ii), Sb(III), Mn, 10^{-9} M Se (VI), Tl(I), Ge, Ga. At concentrations several orders of magnitude higher than those occurring naturally Ga and Sb give peaks at or near the Al potential. High concentrations of Zn cause interference either as a discrete peak slightly positive of the Al peak or as a 'hump' on the Al peak. Interference from high concentration of Zn in fresh waters is overcome by addition of 10^{-4} M EDTA to mask the zinc peak, and preconcentration at -1.0 V (as opposed to -0.8 V). In sea water, preconcentration at -1.0 V (followed by scanning from -0.9 V) is sufficient to overcome interference from zinc. (For modification to the analytical procedure see section G9.12).

G3.5 Variation in peak current with pH

The peak current is stable with respect to pH between pH 8.5 and 5.7. Between pH 5.4 and 5.7 the peak disappears—this coincides with the loss of solution colour due to change in the structure of the reagent. A pH value of 7.1 was chosen as this gives a convenient baseline and good separation on Al peak and H wave. EDTA at up to 2×10^{-4} M has no effect on the Al peak current—however, it does suppress the Zn peak especially in fresh waters.

G4 Hazards

G4.1 Mercury

Mercury is toxic by inhalation and its effects as a poison are cumulative. Great care should therefore be taken in its handling and storage; See A4.1.

G5.1 Redistilled Water

The redistilled water used in the preparation of reagents and for the rinsing of apparatus can best be obtained from a double silica still. The organic content of this water is generally less than that of water produced by deionizers.

G5.2 50% (v/v) Hydrochloric Acid

Dilute 10 ml of ultrapure, 11.4 N hydrochloric acid to 20 ml by addition of redistilled water. It should be prepared freshly weekly, and stored in a polyethylene container.

G5.3 0.1 N Hydrochloric Acid

Dilute 4.4 ml of ultrapure, 11.4 N hydrochloric acid to 500 ml by addition of redistilled water. Store in a polyethylene container and use in the preparation of working standard solutions.

G5.4 1 N Nitric or Hydrochloric Acid

A reagent grade nitric or hydrochloric acid should be diluted with distilled water. Use the solution as an acid wash for soaking the cell, magnetic stirrer, glass pipettes and other glass and plastic ware.

G5.5 Aluminium Standard Solutions

G5.5.1 37.1×10^{-3} M Al Standard 1000 ppm), in 1 N HCl. Dissolve 1.00±0.002 g of aluminium wire in 90 ml of concentrated hydrochloric acid with gentle heating. Cool and dilute the solution quantitatively to a volume of 1 litre. Store the solution in a clean plolyethylene container. Alternatively, commercial standard solutions for atomic absorption spectrophotemetry can be use.

G5.5.2 Suitable Working Standard Solutions are prepared from the above solution by dilution with 0.1 NHCl and are stored in clean polyethylene containers for up to 6 days.

G5.6 Mercury

Triple distilled mercury is used to fill the reservoir of the working electrode. This reagent is hazardous (see section G4).

G5.7 Saturated Potassium Chloride Solution

Shake 25 g of high purity KCl with redistilled water until equilibrium is obtained. Use this solution to fill the salt bridge of the calomel reference electrode.

G5.8 1 M (pH 7.1) BES Buffer Solution

Dissolve 4.265±0.01 g high purity N,N¹-Bis-(2-hydroxyethyl)-2-amino-ethanesulphonic acid in 20 ml 0.5 M sodium hydroxide solution. Adjust to pH 7.1 by cautious addition of 50% (v/v) hydrochloric acid. Store in a clean polyethylene container. Note: This reagent may require treatment to remove Zn impurities. This is best achieved by shaking overnight with 5×10^{-4} M 'MnO_2' suspension (A5.9) and then filtering through a 0.45 μm membrane filter.

G5.9 10^{-3} M DASA Solution

Dissolve 0.0342±0.001 g high purity 1,2-dihydroxyanthraquinone-3-sulphonic acid (DASA) in 100 ml of quartz-distilled water. Store in a clean polyethylene container for up to six days.

G5.10 2.5 M Sodium Hydroxide Solution

Dissolve 10 g high purity sodium hydroxide in quartz distilled water. Transfer the solution to a 100 ml calibrated volummetric flask and dilute to the mark. This solution is stored in a polyethylene container.

G5.11 0.5 M Sodium Hydroxide Solution

Dilute 20 ml of 2.5 M sodium hydroxide solution to 100 ml by addition of redistilled water. Store in a polyethylene container and use in the preparation of the BES buffer solution.

G5.12 10^{-1} M EDTA Solution

Dissolve 3.72±0.02 g EDTA disodium salt in 100 ml of quartz distilled water. Adjust to neutral pH with sodium hydroxide.

G6 Equipment

G6.1 Cleanliness

Where possible, plastic and glassware should be reserved solely for low level Al determinations. Clean all glassware by standing it in 1 N nitric or hydrochloric acid when not in use, and before use wash it with redistilled water several times. Stand the platinum counter electrode, the magnetic stirrer bar and the PTFE bubbling tube in 1 N acid when not in use and before use rinse thoroughly with redistilled water. Stand the calomel reference electrode in 3 M KCl solution, which has been acidified to approximately 0.1 N with 50% (v/v) HCl, when not in use and rinse thoroughly with redistilled water prior to use. After the measurement of each sample rinse the outside of the working electrode glass capillary tube with redistilled water and after use store it either dry (covered) or in redistilled water.

G6.2 A Hanging Mercury Drop Electrode (HMDE)

G6.3 A suitable Polarographic Analyser

G6.4 A good quality X-Y or Y-time Chart Recorder

G6.5 A glass of PTFE Electrochemical Cell which is either readily incorporated as a part of the electrode assembly or has its own sealable polyethylene lid with apertures for working electrode, reference electrode, purge gas bubbling tube platinum counter electrode and pH electrode (optional).

G6.6 Standard Calomel (reference) Electrode (SCE)

The reference electrode is filled with saturated KCl solution to a level such that when the SCE is immersed in the sample solution, the sample solution level is above the level of the KCl solution in the SCE (see figure 2); this is to prevent a net outflow of KCl solution, which may contain significant concentrations of Al to the sample solution. To avoid this form of contamination a double-junction reference electrode is recommended. The outer sleeve is then filled with 0.1 M KCl or with the sample.

G6.7 Platinum Wire Counter Electrode

G6.8 PTFE bubbling tube connected, via a drechsel bottle container redistilled water, via a regulator to a cylinder of inert gas (Ar or N_2).

G6.9 An electronically controlled Magnetic Stirrer

G6.10 A PTFE-coated Magnetic Stirrer Bar

G6.11 A polycarbonate Pressure Filtration Apparatus for use with 47 mm diameter membrane filters (The Sartorius apparatus has been found satisfactory).

G6.12 UV Irradiation Chamber fitted with 1 KW-mercury lamp with concentrically arranged fused silica tubes of 150 ml capacity. (see Fig 28)

G6.13 An Adjustable Micropipette variable between 10 μl and 100 μl

G6.14 A good quality pH Meter and Electrode

G7 Sample Collection

For the collection of surface water samples use clean, acid-washed plastic containers; for sub-surface collections use all-plastic sampling apparatus and suspend it on plastic-coated suspension cable. Care should be taken to avoid the collection of samples close to a ship or close to the exhaust of an outboard motor. In collecting a river or estuarine or tap water sample care should be taken to avoid collecting a non-representative sample.

G8 Pretreatment and Storage of Samples

Immediately after collection, pass the sample (>500 ml) through a 0.45 um membrane filter, which has been washed by soaking in 0.1 N hydrochloric acid and rinsing in redistilled water, using a pressure of about 0.3 bar. Acidify 100±0.2 ml by addition of 100±5 μl of 50% (v/v) HCl. Irradiate the acidified sample for 2–3 hours in a clean silica tube. Store the irradiated sample in a clean PTFE or fused silica container until analysed.

G9 Analytical Procedure

Read section G4 on hazards before starting this procedure.

Step	Procedure

G9.1 Bring 100 ml of the acidified, irradiated sample to neutral pH (7.8 ± 0.4) by addition of 200μl of 2.5 M sodium hydroxide solution.

G9.2 Accurately pipette 10 ml of sample into the electrochemical cell

G9.3 Using a micropipette, add 100 μl of 1 M BES buffer to the sample solution.

G9.4 Using a micropipette, add 100 μl of 10^{-3} M DASA solution to the sample.

G9.5 Place a clean stirrer bar in the cell and put the cell into position on the stand ensuring an airtight seal around the rim.

G9.6 Gently bubble an inert gas (N_2 or Ar) through the sample for 8 minutes (a longer purging time is necessary for larger sample volumes).

G9.7 Set up the polarograph as follows:

Initial potential	−0.09 V
Modulation (pulse) amplitude	25 mV
Scan rate	20 mVs $^{-1}$ (-ve direction)
Drop time	0.1 s
Operating mode	Differential pulse
Low pass filter	Off
Current range	0–0. 5 μA. (a)

(a) Note that lower current range settings than 0.5 μA generally result in increased noise and hence difficulties in measuring peak heights; higher current range settings should be used if higher Al concentrations are expected.

G9.8 Once purging of the sample is complete and the polarograph is set up, adsorption may be commenced. First, the magnetic stirrer and the potentiostat are switched on (b). Once the sample solution is in steady motion adsorption is commenced by extruding a fresh mercury drop (c) and the timer is started. After a fixed adsorption time the stirrer is switched off, and after a further 15s waiting period, during which the chart recorder is activated, the scan is initiated over a current range corresponding to the expected Al concentration and the peak is recorded.

(b) The optimum stirring rate, which gives maximum sensitivity without too much turbulence in the sample solution, must be determined experimentally as it will vary with the shape of the electrochemical cell etc.

(c) The mercury drop used when obtaining the test data had a volume of 3.52 cm^3, a radius of 4.4×10^{-2} cm and a surface area of 2.4×10^{-2} cm^2. Drops of slightly different size would be acceptable provided all drops used during the analysis are identical in size and shape.

G9.9 An appropriate standard addition of Al is then made to the sample with a micropipette and the solution purged with an inert gas for a one minute period. The previous mercury drop is discarded and a further drop is formed and discarded before the working drop is extruded. Repeat the measurement as described in section G9.8

G9.10 A further addition of Al standard is made and section G9.9 repeated.

Step	Procedure
G9.11	The volume of each standard addition should be small, ie 25 μl, so as not to significantly alter the volume of the sample.
G9.12	When Zn is present at high concentration in the sample it causes interference in this determination (see section G3), however, this problem is overcome by adopting the following procedure.
G9.12.1	If the sample is fresh water (ie drinking water, river water etc) add 10 μl of 10^{-1} M EDTA solution to the sample along with the buffer and complexing reagent.
G9.12.2	For both fresh and sea waters proceed with step G9.6 as usual.
G9.12.3	Then with the cell disconnected from the polarograph (ie cell off), activate the recorder and scan from -0.9 V to -1.0 V then using the polarograph's HOLD function hold at -1.0 V. This operation is performed while the sample is being purged.
G9.12.4	Once purging of the sample is complete, and the polarograph has been set up, adsorption may be commenced. First, the magnetic stirrer and potentiostat are switched on. Once the sample solution is in steady motion adsorption is commenced by extruding a fresh mercury drop and the timer is started. After a fixed adsorption time the stirrer is switched off, a period of 10s is allowed to elapse and the potential is then returned to the initial potential (-0.9 V). A further period of 10s is allowed to elapse, during which the recorder is activated, and the scan is initiated over a current range corresponding to the expected concentration and the peak is recorded.
G9.12.5	Standard additions of Al are made and steps H9.12.2–H9.12.4 are repeated. (See figure 22).

G10 Measurement of Peak Heights

The peak heights for the sample and the sample plus standard additions of Al are plotted against the concentrations of added Al standard in the manner illustrated in figure 23. The concentration of Al in the sample is then from the negative portion of the concentration axis.

G11 Sources of Error

The analytical procedure can be applied to samples ranging from ultra-pure water to sea water, but as with most determinations of trace substances, the major source of error is the introduction of contaminants. The ways in which general contamination is avoided vary from laboratory to laboratory, analysts must decide on the precautions appropriate to their requirements. The use of a laminar flow cabinet is recommended. See Section A12.

Leave the cell components to soak in acid when they are not in use, and use the reference cell in the manner described in section G6.6

For error due to interfering substances see section G3.

G12 Effect of Preconcentration Time

The Al peak current increases with adsorption time up to an adsorption time of 3 minutes (see figure 24). At longer adsorption times the Al peak begins to merge with the hydrogen wave.

G13 Checking the Accuracy of Analytical Results

Once the method has been put into routine use the main factor will affect the accuracy of results (apart from contamination) will be operator errors, eg pipetting, peak height measurement etc. The effect of this was assessed by the determination, on six successive days, of Al in a filtered and UV irradiated sea water sample the mean concentration and standard deviation are presented here:

Mean concentration:	11.6×10^{-9} M Al
Standard deviation:	4.9×10^{-10} M al
% standard deviation:	4.2%

(Data obtained at the Department of Oceanography, University of Liverpool).

Table 10

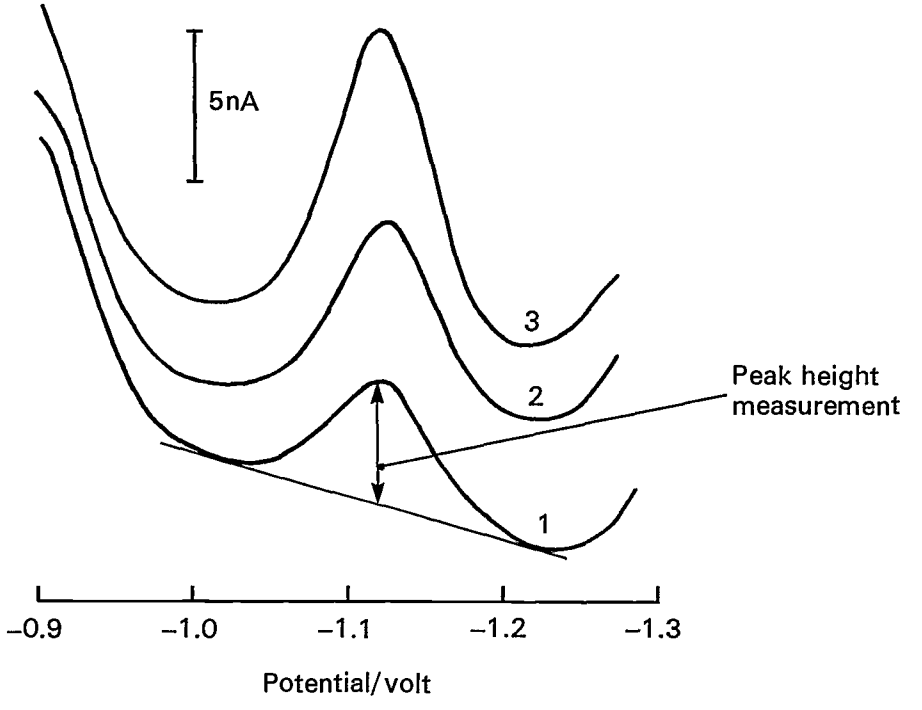
Effect of Triton-X-100 (non-ionic surfactant) on aluminium peak in irradiated sea water; conditions: 10^{-5} M DASA, 0.01 M BES (pH 7.1), 50 mVs^{-1} scan rate, 10 $pulse^{-1}$, 50 mV pulse amplitude, 30s adsorption time, Al concentration 35 nM.

Triton-X-100 concentration mg l^{-1}	Effect on Al peak current as a percentage of original peak
0	0
0.1	−12.5
0.2	−21.4
0.5	−15.4*
1.0	−100

*Peak current apparently increases with 0.5 mg l^{-1}. Triton-X-100. This is due to a broadening of the peak and a negative shift so that it begins to merge with the hydrogen wave.

Figure 22 Differential pulse cathodic stripping voltammetry of Al

Conditions: irradiated sea water, pH 7.1, 10^{-5}M DASA, 20mV s^{-1} scan rate, 10 pulses s^{-1}, 25mV pulse amplitude, −1.0V adsorption potential, scan initiated from −0.9V, 45s adsorption time



Scan 1 : irradiated sea water

Scan 2 : irradiated sea water + 7.4nM Al

Scan 3 : irradiated sea water + 22.2nM Al

Figure 23 Calibration curve for the determination of Al

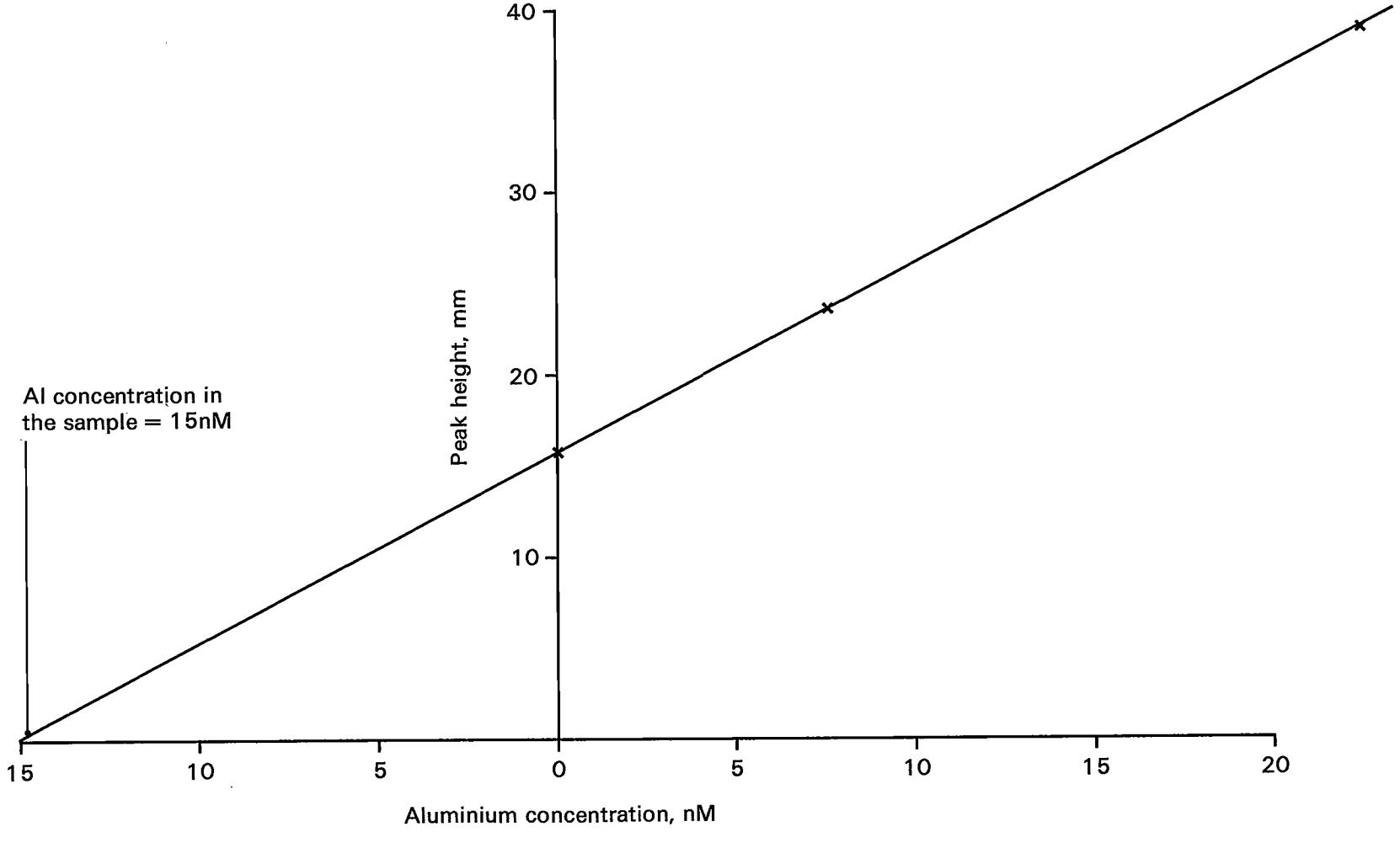
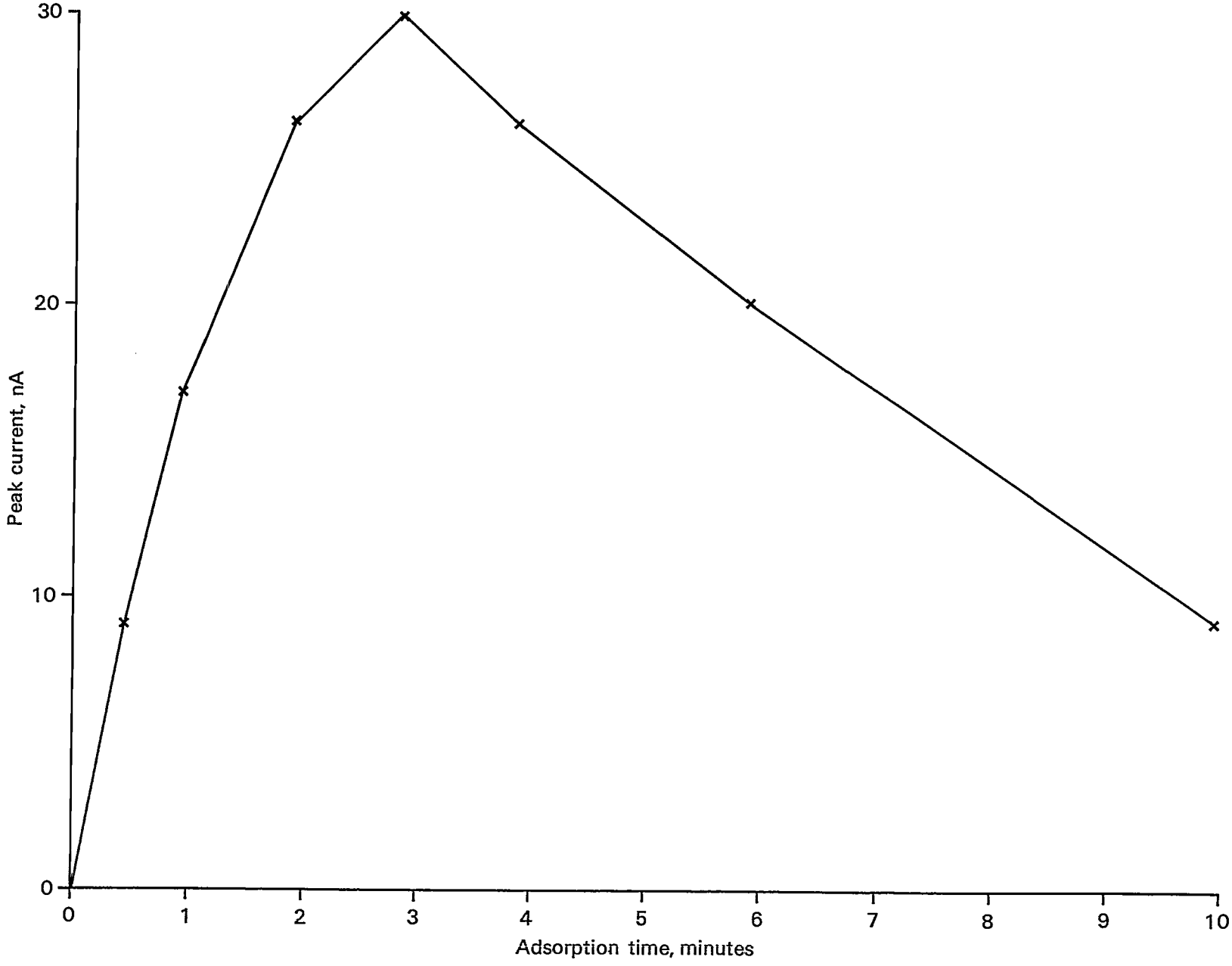


Figure 24 Effect of preconcentration time on peak current

Conditions: irradiated sea water, 40nM Al, pH 7.1, 10^{-5}M DASA



H Direct Determination of Iron in Fresh and Sea Waters by Linear Sweep Cathodic Stripping Voltammetry with the Hanging Mercury Drop Electrode.

H1 Performance Characteristics of the Method

H1.1 Substance determined

Dissolved + colloidal Fe in the 2^+ and 3^+ oxidation states.

H1.2 Type of sample

Sea water and other natural waters.

H1.3 Basis of method

The electrodeposition of the complex formed between iron (III) and 1-nitroso-2-naphthol (1-N-2-N) on the surface of a hanging mercury drop electrode (HMDE), and its subsequent determination by linear sweep cathodic stripping voltammetry (LSCSV).

H1.4 Range of application (a)

Up to 4.0×10^{-8} M (2.3 μg l^{-1}) (b).

H1.5 Calibration curve (a)

Linearity range depends on adsorption time and stirring rate. It is linear up to 4.0×10^{-8} M (2.3 μg l^{-1}) under the stated conditions (b).

H1.6 Total standard deviation (a)

Iron		Concentration	Standard deviation	Degrees of Freedom
(i)	6.0×10^{-9} M	(348 ng l^{-1})	0.36×10^{-9} M (21 ng l^{-1})	10
(ii)	70.5×10^{-9} M	(4.1 μg l^{-1})	2.8×10^{-9} M (162 ng l^{-1})	8

(i) Irradiated seawater.

(ii) Artificial electrolyte solution, 0.05 M sodium chloride, 30s adsorption, −0.1 V adsorption potential

H1.7 Detection limit (a)

1.0×10^{-9} M (58 ng l^{-1}) (c).

H1.8 Sensitivity (a)

10 nM Fe gives a peak current of 10.6 nA after 1 minute preconcentration in sea water. Sensitivity is dependent on stirring rate and can also be affected by interfering substances (see Section H3).

H1.9 Bias

No bias was detected except when interference occurred.

H1.10 Interferences

Certain substances cause interference in the determination of iron (see Section H3).

H1.11 Time required for analysis

The typical time required for the analysis of one sample is approximately 15 minutes; this includes 8 minutes for purging of the sample and approximately 7 minutes for adsorption and scanning of the sample and two standard

additions (when a 1 minute adsorption time is used). The time varies, however, according to the sample volume used because larger sample volumes require longer purging times.

Note: (a) Work carried out at the Department of Oceanography, University of Liverpool.

(b) Several factors can affect the linear response of the determination. The greatest linear range is obtained when the solution is not stirred during the adsorption step and short (eg < 1 minute) adsorption times are used. However, although it is possible to determine higher concentrations of Fe than 10^{-7} M there is a danger of contaminating the electrode and cell components.

(c) Detection limit using a 1 minute adsorption time in irradiated seawater. The detection limit can be reduced by increasing the adsorption time.

H2 Principle

H2.1 The method is based upon the formation of 1-N-2-N complexes of Fe (III) and their adsorption at the hanging mercury drop electrode (HMDE) at a controlled potential of −0.15 V vs a standard calomel reference electrode. (72) The preconcentration is carried out for an accurately measured time period in a solution which is maintained at pH 6.9 by addition of PIPES buffer and which is stirred at a constant rate. Preconcentration, by adsorption, is followed by the analysis step in which the reduction current of the adsorbed complex of Fe (III) is measured by linear sweep cathodic stripping voltammetry (LSCSV).

H2.2 Prior to analysis, the sample is passed through a 0.45 μm membrane filter (see Section H8) to remove particulate material, acidified to pH 2.6 ± 0.2, irradiated and stored in either a quartz or PTFE container.

H2.3 The sample is brought to neutral pH by addition of ammonia solution, the PIPES buffer is added to an aliquot for analysis and the mixture is then purged with inert gas (Ar or N_2) in order to remove oxygen which is an interferent (see Section H3). The sample is initially purged for 8 minutes (10 ml sample volume), or for a longer period for larger sample volumes, and is thereafter purged for 60s prior to subsequent measurements in the same sample solution.

H2.4 The complexing agent, 1-N-2-N, is added and the sample is purged for a further 30s.

H2.5 If all other conditions, (eg instrument settings, stirring rate, pH etc) are kept constant, the sensitivity of the technique is directly dependent on the rate of deposition which is in turn proportional to the rate of diffusion of the complex ions on to the HMDE surface. The diffusion rate is temperature dependent and it is therefore necessary to ensure that the temperature is constant to within ± 0.5°C during a set of measurements (a 0.5°C change in temperature results in variation in the rate of adsorption, and hence of the peak height of 1.5%). No special precautions need to be taken if the sample is at room temperature.

H2.6 Following the adsorption step, the stirrer is switched off and a period of 15s is allowed to elapse, during which the solution comes to rest, before stripping is initiated.

H2.7 Following the 15s waiting time, a potential ramp of 50 mVs^{-1} is applied. The current is recorded and the output is obtained in the form of peaks, with heights proportional to the amount of electroactive species formed in the preconcentration step. The iron peak is at a potential of −0.5 V vs a SCE at a pH of 6.9

H2.8 The concentration of iron in the sample is determined by the method of standard additions.

H3 Interferences

H3.1 Oxygen, surface-active organic material, strong chelating compounds and some dissolved metals cause interference. Oxygen, however, is removed by purging the sample with argon or nitrogen.

H3.2 Surface active organic materials reduce the peak current for Fe slightly. The non-ionic surfactant Triton-X-100 has been previously used as a model for surface active organic material in sea water (41), when it was found that suppression of capacitance on a HMDE by natural surface active organic materials in sea water was similar to that caused by 0.01–0.05 mg l^{-1} of Triton-X 100. The effect of additions of Triton-X-100 to sea water on the iron peak current is shown in Table 11.

H3.3 High concentrations of strong chelating compounds are known to mask some metal/complex reduction peaks. In sea water, at pH 6.9 with 2×10^{-5} M 1-N-2-N and an iron concentration of 19 nM the iron peak current is unaffected by EDTA concentrations up to 10^{-3} M. Natural organic complexing agents are much weaker chelating agents than EDTA and are present in natural waters at far lower concentrations than 10^{-3} M.

H3.4 Metals can interfere potentially in two ways:

(i) as a result of overlapping stripping peaks, and

(ii) as a result of competition from other metal -1-N-2-N complexes for space on the HMDE surface.

H3.4.1 In sea water at pH 6.9 with 2×10^{-5} M 1-N-2-N, nickel produces a peak just positive of that of iron and uranium produces a peak just negative of it. Interference due to uranium does not occur below a concentration of 60 nM, well above those which occur in natural waters. Nickel interference does not occur below nickel concentrations of 100 nM, again much greater than those which occur naturally.

H3.4.2 Additions of 50 nM Cr^{3+}, 50 nM Se^{4+}, 280 nM Mo^{6+}, 300 nM Al, 90 nM In^{3+}, 100 nM Mn^{2+}, 200 nM Ti^{3+} and 100 nM Zn^{2+} caused no diminution of the iron peak.

H4 Hazards

H4.1 Mercury

Mercury is toxic by inhalation and its effects as a poison are cumulative. Great care should therefore be taken in its handling and storage; See A4.1.

H5 Reagents

H5.1 Redistilled Water

The redistilled water used in the preparation of reagents and for the rinsing of apparatus should be obtained from a double silica still. The organic content of this water is generally less than that produced by deionizers.

H5.2 50% (v/v) Hydrochloric Acid

Dilute 10.0 ± 0.2 ml of ultrapure, 11.4 N hydrochloric acid to 20 ml by addition of redistilled water. Prepare afresh each week and store in a polyethylene container.

H5.3 0.1 N Hydrochloric Acid

Dilute 4.4 ml of ultra pure, 11.4 N hydrochloric acid to 500 ml by addition of redistilled water. Store in a polyethylene container and use in the preparation of the working standard solution.

H5.4 1 N Nitric or Hydrochloric Acid

Reagent grade nitric or hydrochloric acid should be diluted with distilled water and used as an acid wash for soaking the cell, magnetic stirrer, glass pipettes and other glass and plastic ware.

H5.5 Standard Iron Solutions

H5.5.1 Iron solution containing 1 mg/ml (17.9×10^{-3} M).

Dissolve 1.000 g ± 0.002 g of metallic iron in 175 ± 1 ml of 50% (v/v) hydrochloric acid. After it has dissolved transfer the solution to a 1l calibrated flask and dilute to the mark with redistilled water. Store the solution in a clean polyethylene container. Alternatively, a 1,000 ppm commercial standard solution for AAS may be used.

H5.5.2 Suitable Working Standard Solutions are prepared from the above solution by dilution with 0.1 N hydrochloric acid and are stored in clean polyethylene containers for up to six days.

H5.6 Mercury

Triple distilled mercury is used to fill the reservoir of the working electrode. This reagent is hazardous (see Section H4).

H5.7 Saturated Potassium Choride Solution

Shake 25 g of high purity KCl with 45 ± 1 ml of redistilled water until equilibrium is attained. Use this solution to fill the salt bridge of the calomel reference electrode.

H5.8 1 M (pH 6.9) PIPES Buffer Solution

Dissolve 6.49 ± 0.01 g high purity piperazine-N, N'-bis-2-ethane sulphonic acid monosodium salt in 20 ml of 0.5 M ammonia solution. Adjust to pH 6.9 ± 0.2 by cautious addition of 50% (v/v) hydrochloric acid. Store in a clean polyethylene container.

H5.9 2×10^{-3} M 1-Nitroso-2-naphthol Solution

Dissolve 0.069 g ± 0.001 g of high purity 1-N-2-N in 200 ml of 0.25 M high purity sodium hydroxide solution. Dissolve by agitation overnight or until the final traces of 1-N-2-N are dissolved. Store in a clean polyethylene container.

H5.10 50% (v/v) Ammonia Solution

Dilute 10.0 ± 0.2 ml of ultrapure, 18 M ammonia solution to 20 ml by addition of redistilled water. Prepare afresh each week and store in a polyethylene container.

H5.11 0.5 M Ammonia Solution

Dilute 2.8 ± 0.1 ml of ultrapure, 18 M ammonia solution to 100 ml by addition of redistilled water. Store in a polyethylene container and use in the preparation of the PIPES buffer solution.

H5.12 4.0 M Sodium Chloride Solution

Dissolve 5.844 ± 0.002 g high purity sodium chloride in redistilled water. Make up to 25 ml volume. Store in a clean polyethylene container.

H6 Equipment

H6.1 Cleanliness

Iron is a very common laboratory contaminant, so where possible, plastic and glassware should be reserved solely for low level Fe determinations. Clean all glassware by standing it in 1 N nitric or hydrochloric acid when not in use, and before use wash it with redistilled water several times. Stand the platinum counter electrode, the magnetic stirrer bar and the PTFE bubbling tube in 1 N acid when not in use and before use rinse thoroughly with redistilled water. Stand the calomel reference electrode, when not in use, in 3 M KCl solution, which has been acidified to approximately 0.1 N with 50% (v/v) HCl, and rinse thoroughly with redistilled water prior to use. After the measurement of each sample rinse the outside of the working electrode glass capillary tube with redistilled water and after use store it either dry (covered) or in redistilled water.

H6.2 A Hanging Mercury Drop Electrode (HMDE)

H6.3 A Suitable Polarographic Analyser

H6.4 A glass or PTFE Electrochemical Cell which is either readily incorporated as part of the electrode assembly or has its own sealable polyethylene lid with apertures for working electrode, reference electrode, purge gas bubbling tube, platinum counter electrode and pH electrode (optional).

H6.5 Standard Calomel (reference) Electrode (SCE)

The reference electrode is filled with saturated KCl solution to a level, such that when the SCE is immersed in the sample solution, the sample solution level is above that of the KCl solution in the SCE (see Figure 2); this is to prevent a net outflow of KCl solution, which may contain significant concentrations of Fe, to the sample solution. To avoid this form of contamination the use of a double-junction reference electrode is recommended. The outer sleeve is then filled with 0.1 M KCl or with the sample.

H6.6 Platinum Wire Counter Electrode

H6.7 PTFE Bubbling Tube connected via a drechsel bottle containing redistilled water, and via a regulator to a cylinder of inert gas (Ar or N_2).

H6.8 An electronically controlled Magnetic Stirrer

H6.9 A PTFE-coated Magnetic Stirrer Bar

H6.10 A polycarbonate Pressure Filtration Apparatus for use with 47 mm diameter membrane filters (the Sartorius apparatus has been found satisfactory).

H6.11 An adjustable Micropipette variable between 10 μl and 100 μl.

H6.12 A good quality pH Meter and Electrode.

H6.13 A 1 kW mercury lamp in a UV Irradiation Chamber with concentrically arranged silica tubes. (see Fig 28).

H7 Sample Collection

For the collection of surface water samples use clean, acid-washed plastic containers; for sub-surface collection use all-plastic sampling apparatus and suspend it on plastic-coated suspension cable. See also H3.4. Care should be taken to avoid the collection of samples close to a ship or close to the exhaust of an outboard motor. In collecting river or estuarine samples care should be taken to collect a representative sample.

H8 Pretreatment and Storage of Samples

Immediately after collection pass the sample (> 500 ml) through a 0.45 μm membrane filter, which has been washed by soaking in 0.1 N hydrochloric acid and rinsing in redistilled water, using a pressure of about 0.3 bar. Acidify the sample to a pH of 2.6 ± 0.2 by addition of 100 ± 5 μl of 50% (v/v) hydrochloric acid to each 100 ml of sample. Irradiate the sample for two–three hours and store it in a clean PTFE or fused silica container.

H9 Analytical Procedure

Read Section H4 on hazards before starting this procedure.

Step	Procedure
H9.1	Add 1.00 ± 0.02 ml of 1 M PIPES solution to 100 ± 1 ml of the acidified sample.
H9.2	While stirring gradually add 75 ± 5 μl of 50% (v/v) ammonia solution to give a pH of 6.9 ± 0.1.
H9.3	Accurately pipette 10 ml of sample into the electrochemical cell.
H9.4	Place a clean stirrer bar in the cell and put the cell into position on the stand ensuring an airtight seal around the rim.
H9.5	Gently bubble an inert gas (N_2 or Ar) through the sample for 8 minutes (a longer purging time is necessary for larger sample volumes).

Step	Procedure

H9.6 Set up the polarograph as follows:

Initial potential	−0.15 V
Scan rate	50 mVs^{-1} (-ve direction)
Drop time	Off
Operating mode	dc
Low pass filter	Off
Current range	0–0.2 μA. (a)

(a) note that lower current range settings than 0.2 μA generally result in increased noise and hence difficulties in measuring peak heights; higher current range settings should be used if higher Fe concentrations are expected.

H9.7 Using a micropipette, add 100 μl of 0.01 M 1-N-2-N solution to the sample and purge for a further 30s.

H9.8 Once purging of the sample is completed and the polarograph has been set up, adsorption may be commenced. First, the magnetic stirrer and the potentiostat are switched on (b). Once the sample solution is in steady motion adsorption is commenced by extruding a fresh mercury drop (c) and the timer is started. After a fixed adsorption time the stirrer is switched off, and after a further 15s waiting period, during which the chart recorder is activated, the scan is initiated over a current range corresponding to the expected Fe concentration and the peak is recorded.

(b) The optimum stirring rate, which gives maximum sensitivity without too much turbulence in the sample solution, must be determined experimentally as it will vary with the shape of the electrochemical cell etc.

(c) The mercury drop used when obtaining the test data had a volume of 3.56×10^{-4} cm^3, a radius of 4.4×10^{-2} cm and a surface area of 2.4×10^{-2} cm^2. Drops of slightly different size would be acceptable provided all drops using during the analysis are identical in size and shape.

H9.9 An appropriate standard addition of Fe is then made to the sample with a micropipette and the solution purged with an inert gas for one minute. The volume of each standard addition should be small, ie < 25 μl, so as not to significantly alter the volume of the sample. The previous mercury drop is discarded and a further drop is formed and discarded before the working drop is extruded. Repeat the measurement as described in Section H9.8 (see Figure 25).

H9.10 A further addition of Fe standard is made and Section H9.9 repeated.

H9.11 Some adjustments may be necessary to the above procedure to combat interference effects (see Section H3). In some freshwaters it may be necessary to add an artificial electrolyte to obtain a well-defined peak current for Fe. If this is necessary then add 125 μl of 4.0 M sodium chloride solution to 10 ml of sample solution to provide an added sodium chloride strength of 0.05 M. Adsorb at a potential of −1.0 V. Iron is present in quite high concentrations in some freshwaters, so to remain within the linear range of the technique it may also be necessary to dilute the sample or to adsorb from an unstirred solution.

H10 Measurement of Peak Heights

The peak heights for the sample plus standard additions of iron are plotted against the concentrations of added iron standard in the manner illustrated in Figure 25. The concentration of iron in the sample is then read from the negative portion of the concentration axis.

H11 Sources of Error

The analytical procedure can be applied to samples ranging from ultra-pure water to sea water, but as with most determinations of trace substances, the major source of error is the introduction of contaminants. The ways in which general contamination is avoided vary from laboratory to laboratory, analysts must decide on the precautions appropriate to their requirements. The use of a laminar flow cabinet is recommended. See Section A12.

Leave the cell components to soak in acid when they are not in use; use the reference cell in the manner described in section H6.6.

For error due to interfering substances see section H3.

H12 Effect of Preconcentration (or adsorption) Time

Measurements of the reduction current as a function of the adsorption time, are shown in figure 27. At elevated iron concentrations the peak current loses linearity earlier as an increasing area of the drop becomes covered with complex ions of Fe and other metals (63).

H13 Checking the Accuracy of Analytical Results

Once the method has been put into routine use the main factor which will affect the accuracy of results (apart from contamination) will be operator errors, eg pipetting, peak height measurement etc. The effect of this was assessed by the determination, on six successive days of iron in a filtered sea water sample. The mean concentration and standard deviation were:

Mean concentration	19.8 nM Fe (1.1 $\mu g\ l^{-1}$)
Standard deviation	1.78 nM Fe (0.10 $\mu g\ l^{-1}$)
% standard deviation	9.1%

(Data obtained at the Department of Oceanography, University of Liverpool).

Table 11

The effect on the iron reduction current of additions of the model surfactant Triton-X-100. Conditions: irradiated sea water, pH 6.9, 2×10^5 M 1-N-2-N.

Added Triton-X-100 (mg l^{-1})	% decrease in Fe reduction current
0.5	7
1.0	9
2.0	10
5.0	46
10.0	66

Figure 25 The reduction of iron — I-N-2-N in sea water

Conditions: 2.0 x 10^{-3} 1-N-2-N, ph 6.9, -0.15V adsorption potential,
1 minute adsorption time

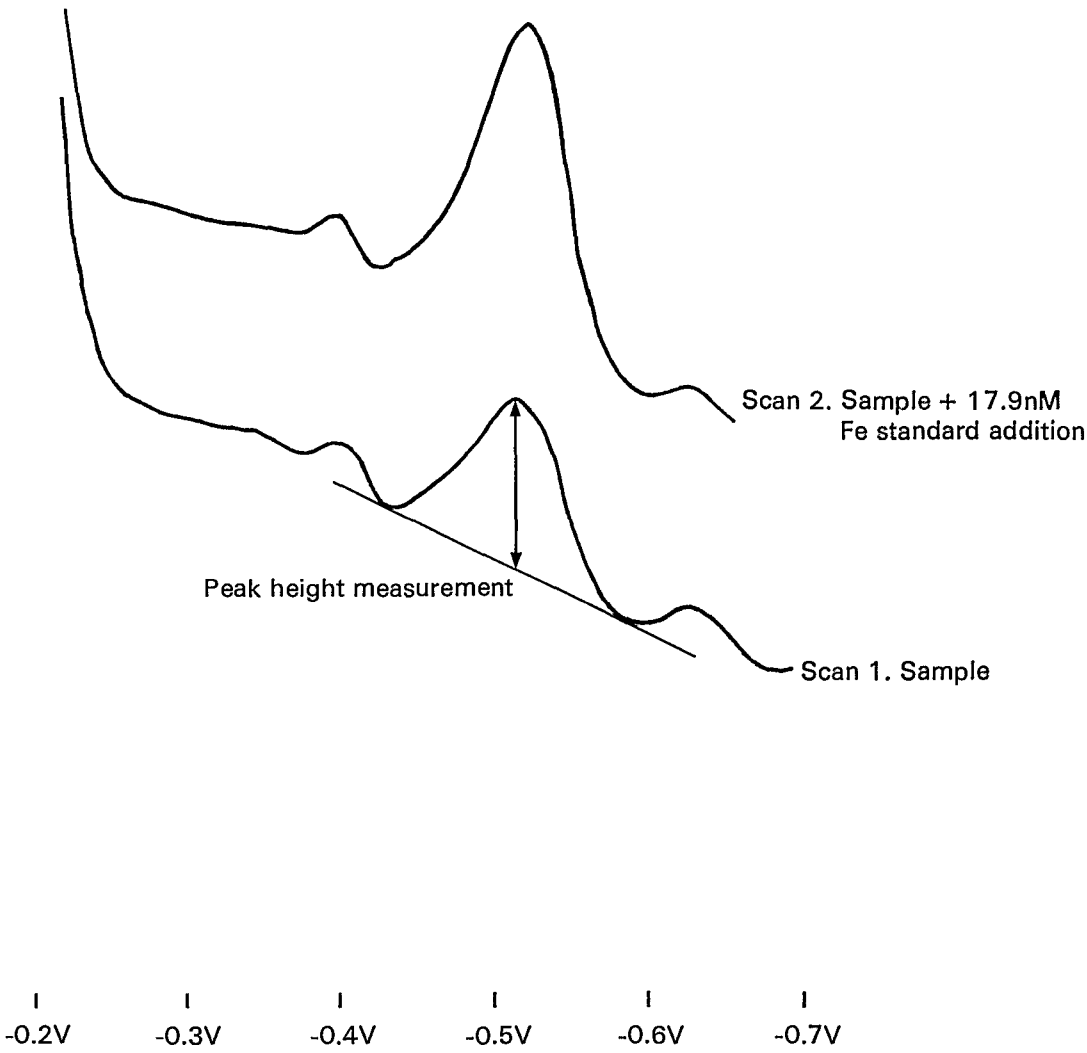


Figure 26 Calibration curve for the determination of iron

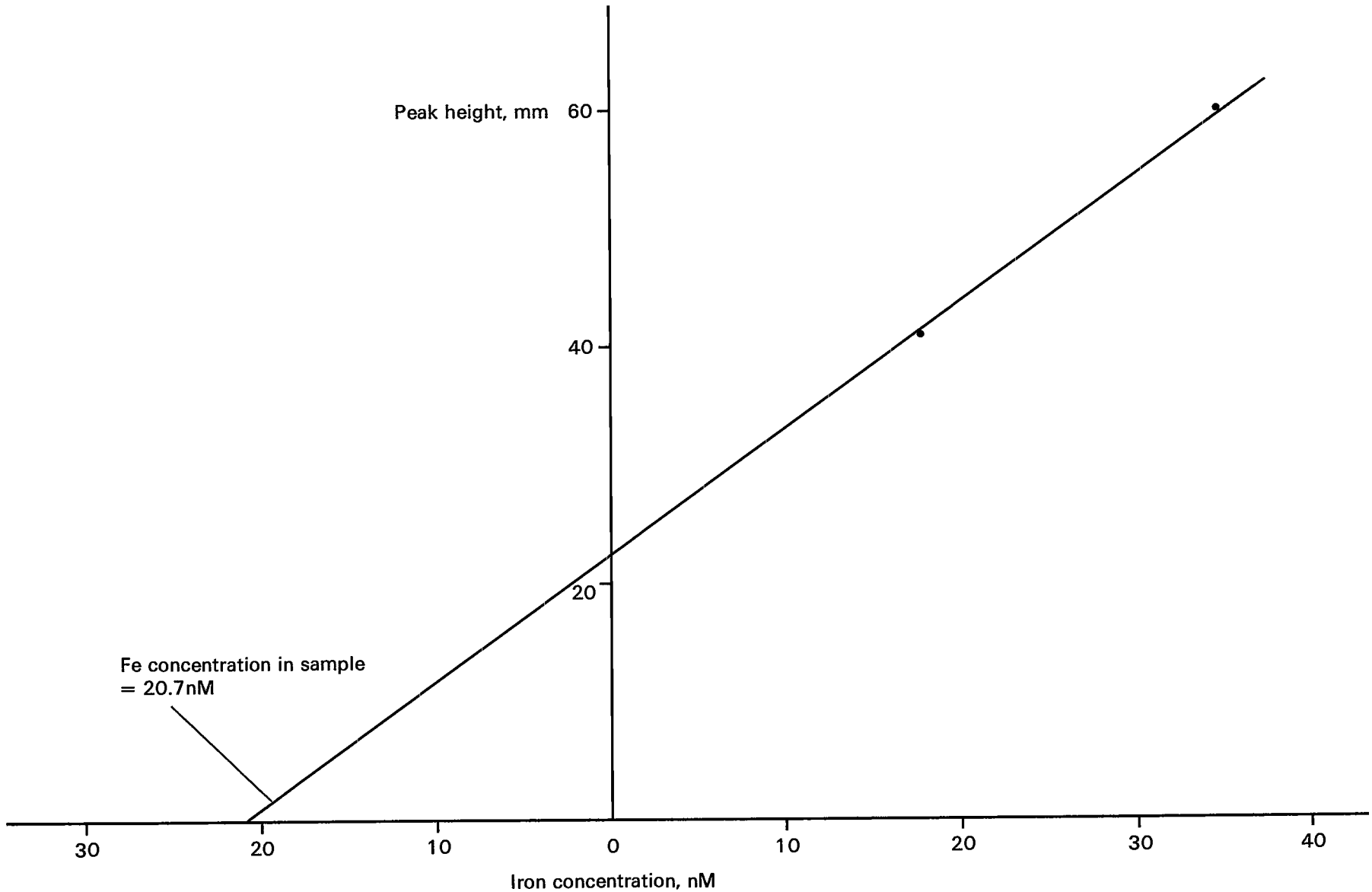
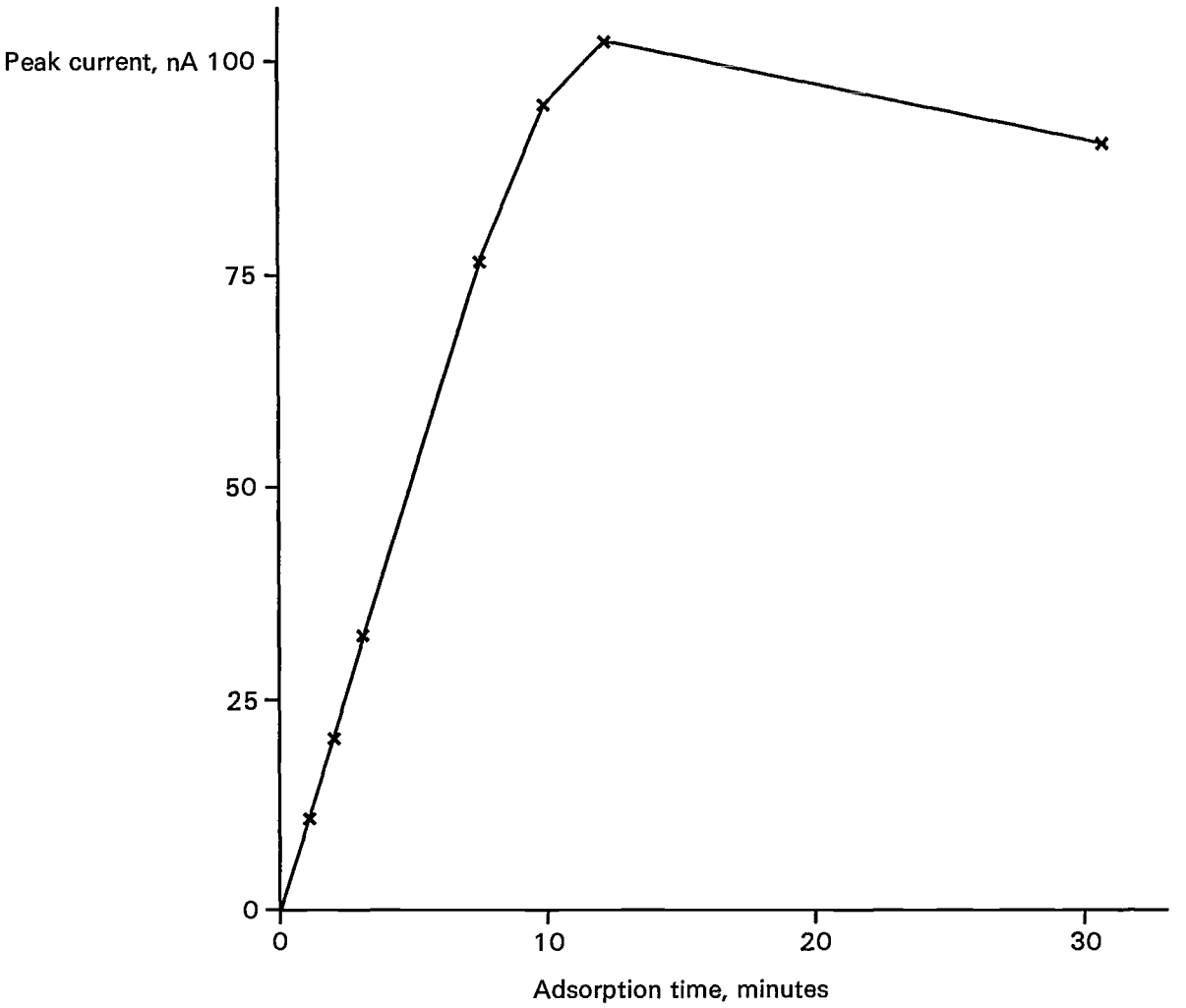


Figure 27 Variation in the iron III peak current with adsorption time

Conditions: Sea water, 38nM Fe, 2 x 10^{-3} 1-N-2-N, pH 6.9



I

The Determination of Dissolved Cadmium, Copper, Lead, Nickel and Zinc in Saline Waters

I1 Performance Characteristics of the Method.

(For further information on the determination and definition of performance characteristics see General Principles of Sampling and Accuracy of Results 1980, also published in this series (1)). (See also refs 35 and 36)

Note: Throughout this method cadmium, copper, lead, nickel and zinc are expressed as the elements, Cd, Cu, Pb, Ni and Zn respectively.

I1.1 Substances determined

'Dissolved' cadmium, copper, lead, nickel and zinc.

For information on particulate analysis see Section I11, on alternative oxidation procedures see Section I12, on the determination of cobalt, iron and manganese, see Section I10.

I1.2 Type of sample

Saline waters (estuarine and coastal waters).

I1.3 Basis of the method

Chelation of dissolved Ni, Cu, Zn, Cd and Pb as dithiocarbamate derivatives, extraction into Freon, back extraction into nitric acid and instrumental analysis by atomic absorption spectrophotometry.

I1.4 Range of application

0 to 0.5 μg Cd/1
0 to 10 μg Cu/1
0 to 5 μg Pb/1
0 to 10 μg Ni/1
0 to 50 μg Zn/1

I1.5 Calibration

Linearity is instrument dependent see ref 19 second part.

I1.6 Total Standard Deviation

Sample	Metal	Concentration found (μg/1)	Standard Deviation S_t (μg/1)	Degrees of Freedon
	Cadmium			
Deionized water (DW)		0.001	0.023	2
DW + 0.05 μg/1		0.043	0.010	8
DW + 0.50 μg/1		0.486	0.021	10
DW + 0.75 μg/1		0.740	0.045	9
Estuarine Water		0.300	0.022	8
Sea water (SW)		0.042	0.013	5
SW + 0.75 μg/1		0.821	0.041	4
	Copper			
DW		0.04	0.21	5
DW + 1 μg/1		1.21	0.25	7
DW + 10 μg/1		9.90	0.25	3
DW + 15 μg/1		15.58	0.68	6
Estuarine Water		4.64	0.29	7
Sea Water		0.53	0.16	3
SW + 15 μg/1		15.54	0.69	3

Lead			
DW	0.36	0.46	7
DW + 1 μg/l	1.30	0.25	10
DW + 10 μg/l	10.10	0.41	10
DW + 15 μg/l	15.83	0.81	10
Estuarine Water	1.36	0.26	6
Sea Water	0.33	0.18	8
SW + 7.5 μg/l	7.88	0.39	6
Nickel			
DW	0.08	0.10	5
DW + 1 μg/l	1.20	0.15	10
DW + 10 μg/l	9.87	0.24	9
DW + 15 μg/l	15.53	0.62	6
Estuarine Water	3.05	0.15	8
Sea Water	0.43	0.10	8
SW + 15 μg/l	15.54	0.33	6
Zinc			
DW	0.73	0.59	5
DW + 5 μg/l	6.08	0.64	10
DW + 50 μg/l	49.32	1.36	4
DW + 75 μg/l	76.39	2.22	9
Estuarine Water	30.84	0.64	9
Sea Water	1.15	0.47	8
SW + 60 μg/l	60.05	2.53	4

I1.7 Limit of detection

Metal	Limit of detection (μg/l)	Degrees of freedom
Cadmium	0.035	10
Copper	0.65	10
Lead	0.75	10
Nickel	0.50	10
Zinc	2.62	5

Note: These limits are above the levels found in most clean sea waters and ocean waters.

I1.8 Sensitivity

Metal	concentration		Absorbance
Cadmium	50 pg	injected into the furnace	0.25
Copper	1000 pg		0.30
Lead	1000 pg		0.23
Nickel	2000 pg		0.23
Zinc	500 μg/l	(in extract)	0.25

I1.9 Bias

None detected

I1.10 Interferences

See section I3

I1.11 Time required for analysis

Total analytical time for 20 samples—3 days consisting of

pretreatment	6 hrs total, c3hrs operator time
extraction	6 hrs, all operator time
EAAS	c7hrs total, 1½ hrs operator time
AAS (Zn)	75 mins, all operator time
	some simultaneous operation is possible.

I2 Principle

'Dissolved' cadmium, copper, lead, nickel and zinc, that is the concentration of these metals in a sample which has been filtered through a 0.45 μm filter, are determined following oxidative pretreatment using ozone. The metals are concentrated by complexation with a mixed dithiocarbamate reagent and solvent extraction (39), back extracted into nitric acid and then determined by electrothermal (Cd, Cu, Pb, Ni) or flame (Zn) atomic absorption spectrophotometry. For information on the analysis of particular matter see Section I11. For information on the determination of cobalt iron and manganese see Section I10.

I3 Interferences

Complexation of trace metals by organic macromolecules, and the presence of discrete organometallic compounds in natural waters, may result in incomplete recovery of elements of interest from samples. It is therefore necessary to apply an oxidative pretreatment to decompose organic metal compounds and complexes, rendering the metals accessible to the chelating agent. In the present procedure this is achieved by bubbling ozone through acidified samples for 20 minutes. Alternative pretreatments, using ultraviolet irradiation or peroxodisulphate, may also be applicable, but performance data for these are not available. See section I12.

Citrate complexes iron and prevents it reacting with the substituted dithiocarbamates. Cyanide will similarly prevent copper extracting, ethylenediaminetetraacetic acid prevents all metals except copper and silver being extracted. These and other similar complexants, which might interfere with the formation of the various dithiocarbamates, can be removed by any of the oxidation procedures given in I8.2, or I12 prior to carrying out the extraction procedure.

I4 Hazards

The fumes from the atomic absorption spectrophotometer are toxic and must be ducted away. Ozone is toxic and it is essential that the gas stream is vented to a fume hood during the sample pretreatment state.

I5 Reagents

I5.1 Water

Deionized or redistilled water should be used for preparing blanks, standards and reagent solutions. The trace metal content of this water should be negligible compared with the lowest concentration to be determined in the samples.

I5.2 Ammonium Acetate Buffer Solution (2 M acetate)

Add 24.00±0.25 ml of acetic acid (BDH 'Aristar' grade or equivalent d_{20} 1.048) to approximately 50 ml water in a volumetric flask. Carefully add 60±0.8 ml of 35% ammonia solution (BDH 'Aristar' grade or equivalent) swirling the mixture. Dilute to approximately 200 ml with water. This solution should be freshly prepared for each set of extractions.

I5.3 1,1,2-trichloro-1,2,2-trifluorethane

(Freon), GPR.

I5.4 Chelating Agent Solution

(1% w/v in both ammonium pyrrolidine dithiocarbamate and diethylammonium diethyldithiocarbamate)

Dissolve 1.00±0.01 mg of each of ammonium pyrrolidine dithiocarbamate (APDC) and diethylammonium diethyldithiocarbamate (DDDC) in approximately 50 ml water in a 100 ml volumetric flask and dilute to the mark. (Not all the solid will dissolve, however, total dissolution will be achieved during the purification stage.) Transfer the solution to a 250 ml separatory funnel and rinse the volumetric flask with 100 ml 1,1,2 triclorotrifluoroethane (Freon, GPR). Transfer the Freon to the separatory funnel and extract the aqueous solution for approximately 1 minute venting the flask frequently. Allow the phases to separate for 5 minutes, drain the lower organic layer and discard the Freon. Repeat with a second 100 ml portion of Freon. After allowing the phases to separate, drain and discard the organic layer and collect the purified chelating solution in a pre-cleaned 250 ml polyethylene bottle. The reagent should be freshly prepared for each batch of extractions.

I5.5 Mixed reagent solution

Combine 60.0±0.8 ml of chelating agent solution (I5.4) and 120.0 (±1.5 ml buffer solution (I5.2) in a precleaned 250 ml polyethylene bottle. Prepare afresh for each batch of samples.

I5.6 Acid Back Extractant

Concentrated nitric acid (BDH Aristar grade or equivalent d_{20} 1.41).

I5.7 Humic Acid Solutions (for testing the ozone oxidation)

Stock Solution (100 mg/1)
Dissolve 100± mg humic acid in approximately 200 ml of water containing a few pellets of sodium hydroxide. Dilute to 1 litre with water.

Working Solution (approximately 10 mg/1)
Mix 25±0.5 ml stock humic acid solution, 225±2 ml water and 1.25±0.05 ml concentrated nitric acid in a 500 ml Drechsel bottle and mix well.

I5.8 Standard Solution

Standard solutions are prepared daily from commercially available 1000 mg/1 AAS standards.

Solution A (10000 μg Cd/1)
To a 100 ml volumetric flask containing approximately 50 ml water add 1000±2 ul 1000 mg Cd/1 stock standard solution, dilute to the mark with water and mix well.

Solution B (2000 μg Ni/1; 2000 μg Cu/1: 10000 μg Zn/1; 1000 μg Cd/1; 1000 μg Pb/1)

To a 100 ml volumetric flask containing approximately 50 ml water add the following:

1000 ±2 μl Solution A
200 ±0.4 μl 1000 mg Ni/1 stock standard solution
200 ±0.4 μl 1000 mg Cu/1 stock standard solution
1000 ±2 μl 1000 mg Zn/1 stock standard solution
200 ±0.2 μl 1000 mg Pb/1 stock standard solution
Dilute to the mark with water and mix well.

I5.9 pH Adjustment Solution

18% (v/v) Hydrochloric Acid—Add 10 +1ml of concentrated HCl (BDH Aristar grade or equivalent, d_{20} 1.18) to 82± 1 ml of water and mix thoroughly.

17.5% (v/v) Ammonia Solution—Add 50% ±1 ml of 35% ammonia solution (BDH Aristar grade or equivalent, d_{20} 0.88) to 50±1 ml of water and mix thoroughly.

I5.10 Oxygen (oil free)

I5.11 Nitrogen (oil free)

I6 Apparatus

I6.1 Atomic Absorption Spectrophotometer

Any commercially available atomic absorption spectrophotometer equipped for both conventional flame and graphite furnace determinations and preferably with autosampler, background correction and printer attachments is suitable. Instrumental parameters should be set up according to the manufacturer's instructions.

The graphite furnace programmes used to obtain the test data were as follows. Different equipment may require slight variation. Users should ascertain the optimum settings for their own equipment.

Nickel: sample volume = 20 μl

Step	Temp °C	Ramp s	Hold s	Gas flow ml/min	Functions
1	110	5	20	300	
2	1100	10	10	300	BOC at 15 s
3	2700	mp	3	0	Recorder On, Read 3 s
4	2800	3	1	300	Recorder On

Copper: Sample volume = 10 μl

Step	Temp °C	Ramp s	Hold s	Gas/flow ml/min	Functions
1	110	5	20	300	
2	900	10	10	300	BOC at 15 s
3	2250	mp	3	30	Recorder On, Read 3 s
4	2500	3	1	300	Recorder On

Lead: Sample volume = 20 μl

Step	Temp °C	Ramp s	Hold s	Gas/flow ml/min	Functions
1	110	5	20	300	
2	400	10	10	300	BOC at 15 s
3	1100	mp	3	30	Recorder On, Read 3 s
4	2100	3	1	300	Recorder On

Cadmium: Sample Volume = 10 μl

Step	Temp °C	Ramp s	Hold s	Gas/flow ml/min	Function
1	110	5	20	300	
2	250	10	10	300	BOC at 15 s
3	1100	mp	3	0	Recorder On, Read 3 s
4	2100	3	1	300	Recorder On

Note: BOC = Baseline Offset Correction
mp = 'max power' setting

I6.2 Ozone Generator

Ozone is produced using a commercially available laboratory ozonator such as Wallace and Tiernan Model BA.023.

I6.3 Chemical Work Station

Solvent extraction procedures are performed in a clean air Chemical Work Station. The cabinet combines vertical downflow laminar air conditions (Class 100) coupled with fume extraction. This represents ideal conditions for the work providing minimal risk of contamination from airborne particles while ensuring operator safety.

I6.4 Chemical Apparatus

It is strongly recommended that once chemical apparatus has been cleaned it is used solely for trace metal determinations. It is further recommended that apparatus is assigned to a specific task in the method. Where possible apparatus should be made of an appropriate plastic material. Conventional, ie soft polyethylene—non linear, polypropylene and FEP Teflon are all suitable. Closures containing filler should be avoided. Clean apparatus initially by filling or soaking it with 10% v/v nitric acid for at least 48 hours and then rinsing thoroughly with water. Thereafter, a thorough rinse with water and, where appropriate, approximately 10 ml of Freon. Apparatus which comes into contact with solvent (separating funnels and extract bottles) should be stored containing 10 ml Freon in order to avoid drying out.

I7 Sample Collection and Preservation

The sample must be collected in accordance with the advice given in the Introduction, Section I2. Great care must be taken to avoid contamination during the sampling procedure. The sample must be filtered as soon as possible after collection and certainly within the same working day so as to minimize any changes in the particulate: dissolved metal ratios. Filtration must be carried out in a clean working environment and the filtered sample should be preserved at pH<2. For the present method this is achieved by

the addition of 5 ml concentrated nitric acid per litre of sample, the acid being of at least BDH Aristar grade (or equivalent).

I7.1 If analysis of the particulate matter which may contain absorbed metals is required (38) see Section I11.

I8 Analytical Procedure

READ SECTION I4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

I8.1 Batch structure

Up to 20 samples, including one duplicate determination and one unspiked and one spiked control sample, plus four standards and two blanks can be analysed in one batch. The order of samples in the batch should be randomized.

Step	Procedure	Notes
I8.2	**Pretreatment**	
I8.2.1	Prepare the humic acid test solution and measure its UV absorbance at 350 nm.	Steps I8.2.1 to I8.2.5 are intended to check that the ozone oxidation stage is working properly. If the results are not up to the standard required in note (a) investigate the cause and rectify before oxidizing samples starting at I8.2.6.
I8.2.2	Connect the Drechsel bottle to the oxygen supply, turn the gas on and adjust the flow to 100 l h^{-1}. Switch on the ozonator and increase the primary voltage to 230 V.	
I8.2.3	Pass ozone through the solution for 15 min. The solution should lose colour.	
I8.2.4	Switch off the ozonator and disconnect the oxygen supply. Bubble nitrogen through the digested sample for 5 min.	
I8.2.5	Measure the UV absorbance of the test solution (note a).	(a) After 15 min the UV absorbance should have decreased to at least 30% of its initial value.
I8.2.6	After shaking the sample bottle thoroughly, rinse the measuring cylinder and decant 200±0.5 ml of sample. Transfer the sample to a Dreschel bottle and affix a label.	
I8.2.7	Link two Dreschel bottles in series with the oxygen flow and ozonate for 30 min (note b).	(b) O_2 flow of 100 l h^{-1} is recommended.
I8.2.8	After pretreatment disconnect the bottles from the oxygen supply, connect the nitrogen supply and flush for 5 min. Remove and stopper the bottles and set aside for extraction (note c).	(c) N_2 flow of 100 l h^{-1} is recommended.
I8.2.9	Repeat steps I8.2.6 to I8.2.8 for all samples.	
I8.3	**Chelation/solvent extraction**	
	Sample extraction	
I8.3.1	Transfer the 200 ml sample from the Drechsel bottle to a separatory funnel.	
I8.3.2	Add 7.5±0.1 ml of mixed reagent to bring the pH to approximately 4.5.	

Step	Procedure	Notes
I8.3.3	Check the pH value by spotting solution onto a suitable indicator strip and, if necessary, adjust to pH 4.4 to 5.3 (note d). This is essential.	(d) Merck 'Acilit' indicator papers or similar can be used.
I8.3.4	To the buffered sample add 10±0.1 ml of Freon and extract for 2 min±10 s venting the separatory funnel carefully (note e).	(e) To avoid entrainment of droplets of the aqueous phase in the bore of the stopcock, the funnel should be vented only through the top.
I8.3.5	Allow the phases to separate for at least 5 min. Drain the organic layer containing the metal chelates (the lower layer) into a small (50 ml is suitable) polyethylene bottle (note f).	(f) The separation can be stopped before the interface is reached to prevent carry through of salt.
I8.3.6	Immediately add 500±1 µl concentrated nitric acid to the organic layer to initiate decomposition of the chelates, and shake vigorously for 20±5 s	
I8.3.7	Repeat the extraction of the aqueous layer from I8.3.4 with a further 10 ml portion of Freon, shaking for 30±5 s	
I8.3.8	Allow the phases to separate for at least 5 min.	
I8.3.9	Drain the organic layer, combine with the first extract from I8.3.6 and shake thoroughly.	
I8.3.10	Repeat steps I8.3.7 to I8.3.9. Keep a sufficient stock of triply extracted see water See I&.3.12.	
I8.3.11	Add 20±0.03 ml water to the combined organic extracts and mix thoroughly (note g).	(g) It is not necessary to separate the combined Freon extracts from the diluted extracts. Aliquots for analysis can be pipetted directly from the small sample containers. At least 1 h should elapse between extraction and AAS analysis.
I8.3.12	Retain at least 6×200 ml aliquots of extracted seawater for I8.3.10 in an appropriate container for later use as a matrix for the standards.	
	Standards extraction	
I8.3.13	From the combined matrix decant six 200 ml portions into cleaned separatory funnels.	
I8.3.14	Assign two of the solutions as blanks and to the other four solutions make the following additions of Solution B (see Section I5.8): Standard 1—250±0.5 µl Standard 2—500±1 µl Standard 3—750±1.5 µl Standard 4—1000±2.0 µl (note h)	(h) These additions give the following concentrations: (Standard 1) 250 µl 2.50 µg Cu/1 12.50 µg Zn/1 0.125 µg Cd/1 1.25 µg Pb/1 (Standard 2) 500 µl 5.00 µg Ni/1 5.00 µg Cu/1 25.00 µg Zn/1 0.250 µg Cd/1 2.50 µg Pb/1

Step	Procedure	Notes
		(Standard 3) 750 µl 7.50 µg Ni/1 7.50 µg Cu/1 37.50 µg Zn/1 0.375 µg Cd/1 3.75 µg Pb/1 (Standard 4) 1000 µg— 10.00 µg Ni/1 10.00 µg Cu/1 50.00 µg Zn/1 0.500 µg Cd/1 5.00 µg Pb/1
I8.3.15	To each solution add 2.5±0.1 ml chelating agent solution (note i).	(i) No buffer solution is required as the matrix is already at the correct pH.
I8.3.16	Perform the extraction, following steps I8.3.4 to I8.3.11.	

I8.4 Analysis of samples

Analyse equal volumes of samples, blanks controls and standards. Set up the instrument according to the manufacturer's instructions for the determination of each metal in turn using either flame (Zn) or electrothermal atomization (Cd, Cr, Ni, Pb) both with automatic background correction. Recommended settings are given in Section I6.1. The wavelengths required are

cadmium	228.8 nm
copper	324.7 nm
lead	283.3 nm or 217.0 nm
nickel	232.0 nm
zinc	213.9 nm

I8.4.1 A typical order of analysis which has been used is:

Test no.	Solution
1–2	Blanks
3–6	Standard solutions in ascending order
7–26	Samples 1–20 (including controls) in random order
27–28	Blanks
29–32	Standard solutions in ascending order

Preferably, samples are analysed at least in duplicate.

I8.5 Calculation of results

I8.5.1 For each element construct a calibration curve of absorbance versus concentration of standards (note j)

(j) The mean value of the absorbance recorded at the beginning and the end of each run should be plotted. The calibration line should be constrained to pass through the mean blank absorbance value.

I8.5.2 Use the calibration curve to calculate the concentration of that element in the samples.

I9 Sources of Error

In many routine applications the concentrations of dissolved nickel, copper, zinc, cadmium and lead will be very low, so contamination presents a potential problem. The degree of this problem is likely to be greater for some of the elements, especially zinc and lead. Working conditions should therefore be critically examined and precautions taken to minimize this risk.

The only other error which could be expected results from poor separation of the organic and aqueous phases after extraction and trapping of saline matrix in the drain cock of the separatory funnel. Careful manipulation according to the above instructions should avoid this problem.

I10 Determination of Cobalt, Iron and Manganese

These metals can also be determined by this procedure; but complete test data are not available and may be instrument dependent.

	Range of Application	Limit of Detection	Reference for wavelength used
Cobalt	up to 5 μg/l	c 1 μg/l	22,23
Iron	up to 20 μg/l	c 1 μg/l	22,37
Manganese	up to 30 μg/l	c 2 μg/l	22,37

Extra chelating agent (I5.4) should be added and the extractions performed without delay if manganese is sought (the Mn complex is not stable).

I11 Analysis of Particulate Matter (from I7.1)

I11.1 Reagents

I11.1.1 3:1 Hydrochloric Acid/Nitric Acid Mixture.

Immediately before use mix together 3 parts by volume of hydrochloric acid (d_{20} 1.18) and 1 part nitric acid (d_{20} 1.42). Store in a covered, but not stoppered, container in a fume extraction cupboard.

I11.2 Apparatus

I11.2.1 Membrane Filtration Apparatus

The filtration apparatus consists of a Nalgene separating funnel, to the outlet of which a Millipore Swinnex 47 mm filter holder is attached by a short length of silicone tubing. The top of the funnel should be attached to a filtered air or nitrogen supply capable of applying a pressure of 5–10 psi. 47 mm Oxoid or Millipore filter membranes should be cleaned by soaking them in 0.5 M hydrochloric acid for 24 hours, thoroughly washed with distilled water and dried at 50°C in an oven. Nuclepore filters, which do not require acid washing, should be used if particulate trace metals are to be determined. It should be noted that Oxoid or Millipore filters may contain high and variable amounts of zinc. To ensure that the filters are acceptably low in metals, after washing as above, a selected number should be analysed by the method for particulate metals (step I11.4).

I11.2.2 Apparatus for Acid Extraction of Particulate Material

A 250 ml PTFE Beaker with PTFE Clock Glass. This is cleaned by refluxing with the acid mixture and rinsing with distilled water.

I11.2.3 Alternatively, a 100 ml Pyrex conical flask with ground glass neck, fitted with 130 mm long B24–29 ground glass cone to act as an air condenser and splash collector, cleaned as above can be used; but the risk of metal pick up is increased.

I11.3 Filtration step

Note that when the suspended solids load needs to be determined it is desirable to take a separate sample for this, since the handling of the membrane during weighing is a possible source of contamination for the subsequent particulate metals determination.

Step	Procedure	Notes
	Determination of suspended solids	
I11.3.1	Weigh the clean dry filter membranes and store in individual polystyrene petri dishes. Let the weight of a membrane be W_1 mg (note a).	(a) Use an anti-static disc (see Introduction, Section 3.5). Either record the weight on the petri dish, or use prenumbered, predried (as in I11.3.5),

Step	Procedure	Notes
		preweighed petri dishes to reduce handling of used membranes later.
I11.3.2	Transfer a membrane to the Swinnex filter using plastic forceps.	
I11.3.3	Transfer an appropriate aliquot of the saline water, depending on the suspended solids load, to the Nalgene separating funnel and pressurize to 5–10 psi. (note b). Collect the filtrate in a clean dry sample storage bottle. Note the volume, Vml, filtered.	(b) Do not use higher pressures since disruption of phytoplankton cells may release particulate metals.
I11.3.4	Remove the storage bottle. If the filtrate is to be stored before analysis, add sufficient nitric acid (d_{20} 1.42) to lower the pH value to less than 1.5 1.00±0.05 ml of nitric acid per litre of filtrate is usually sufficient. If the procedure used in Section I8 is used, add 5.00±0.05 ml of nitric acid (d_{20} 1.42) per litre Reserve for either steps I8.2.6 to I8.2.9, I12.1 or I12.2.	
I11.3.5	Wash the funnel and membrane with 50±1 ml of distilled water. Discard the washings. Remove the membrane, store in the petri dish, dry at 50±20°C in an oven (or at ambient temperature in a laminar flow hood).	
I11.3.6	Reweigh the dried used membrane. Let the weight be W_2 mg. Reserve for step I11.4 (The membrane is usually removed from the dish and weighed; but if necessary it may be reweighed in the preweighed dish—see note a).	
I11.3.7	Rinse the rig with water and thoroughly drain before further use.	
I11.3.8	Calculate the suspended solids load (SSL) from $\text{SSL} = \frac{W_2 - W_1}{V} \times 1000 \text{ mg/l}.$	
I11.3.9	If the suspended solids load is not required it is only necessary to carry out steps I11.3.1 to I11.3.3 (omitting the weighing stage). Otherwise a separate aliquot of the sample should be filtered to obtain a membrane for 'particulate' metals analysis (note c).	(c) Store the membrane in the petri dish until required for analysis.

I11.4 Extraction of 'Particulate' metals

Step	Procedure	Notes
I11.4.1	Transfer the filter membrane with the particulate material to a clean extraction apparatus (see Section I11.2.2 or I11.2.3). Add 10±1 ml of the 3:1 hydrochloric acid/nitric acid mixture and when any reaction has subsided, place on a clean hot plate at a temperature such that the solution gently simmers (note d). Leave to stand for 3–4 hours.	(d) Cover the hot plate with aluminium baking foil to prevent contamination.

Step	Procedure	Notes
I11.4.2	Evaporate to 2–3 ml (note e). Add 10.0±0.1 ml of hydrochloric acid (d_{20} 1.18) and evaporate again to 2–3 ml. Cool and dilute with 0.5 N hydrochloric acid to a suitable volume for analysis (note f).	(e) Do not allow to go dry. (f) The volume depends on the amount of metals in the material.
I11.4.3	A blank must be run with each batch of determinations in an identical manner to that for the membrane.	
I11.4.4	At least one quality control standard must be run with each batch of determinations in an identical manner to that for the membrane.	
I11.4.5	If necessary, the pH of the sample is brought to <1, by the addition of nitric acid (d_{20} 1.42)	
I11.4.6	Proceed to the atomic absorption stage (step I8.4).	

I12 Alternative Oxidation Procedures

Oxidative pretreatment is generally necessary to remove organic substances and to convert the metals to analytically available forms. This may not always be necessary, particularly for waters of high salinity. Carrying out the determinations with, and without, the oxidation step will indicate to analysts whether oxidation is necessary for their particular types of samples. If the oxidation step can be avoided, this reduces the possibility of contamination by the reagents. (Ni and Co determinations always require oxidation.)

The test data given in Section I1 was obtained using ozonation I8.2. However the following alternative procedures I12.1 and I12.2 have been used in some laboratories. Some adaption may be necessary, especially pH adjustment, prior to extraction. The use of the correct extraction pH is absolutely essential (39). Users of these variants should evaluate their procedure prior to routine use. A variant of I12.1 is given in A8 (see I12.1.4).

I12.1 Ultra Violet—Oxygen Oxidation

I12.1.1 Reagents

I12.1.1.1 2 M Nitric Acid (approximately)

Dilute 125±5 ml of nitric acid (d_{20} 1.42) with water to 1 litre. This reagent is stable for at least 3 months.

I12.1.1.2 2 M Ammonium Hydroxide (approximately)

Dilute 250±5 ml of isothermally distilled ammonium hydroxide (d_{20} 0.94) or 8.5 M, see Introduction 6.2.2) with water to 1 litre. Stored in a stoppered bottle, this solution is stable for at least three months.

I12.1.1.3 3% m/m Hydrogen Peroxide (10 volumes).

Dilute 10.0±0.1 ml of 30% m/m hydrogen peroxide (100 volume) with water to 100 ml. This reagent should be freshly prepared each week.

I12.1.2 Apparatus

The apparatus is shown dramatically in figure 28. It consists basically of a cylindrical aluminium box containing an axially mounted 1 KW medium pressure mercury lamp around which are arranged ten 25 cm diameter fused silica photolysis tubes, each at a distance of 10 cm from the lamp. Cooling, to the optimum temperature of 50±3°C, is provided by an externally mounted fan and the expelled air is vented to a fume cupboard to remove ozone which is toxic at the concentrations encountered. The lid of the photolysis apparatus is fitted with an interlocked micro-switch so that the mercury lamp cannot be operated when the lid is open.

I12.1.3 Ultra Violet-Oxygen Oxidation Procedure

For a flame AAS finish it is necessary to oxidize 1000 ml of sample; but for an electrothermal atomization AAS finish smaller volumes are sufficient. Using a pH meter adjust the pH of up to 1000±10 ml of the filtered sample to pH 6.0±0.3 by cautious addition of 2 M nitric acid, or 2 M ammonium hydroxide if the filtrate had been acidified in step I11.3.4.

Transfer the solution to sufficient 25 × 4 cm silica tubes and loosely stopper. Irradiate for 2 hours in the photolysis apparatus adjusting the flow of air from the fan by means of the butterfly valve (see figure 28) so that an optimum solution temperature of 60±3°C is achieved.

Add 0.25±0.05 ml of 3% m/V hydrogen peroxide solution to each tube to dissolve any precipitated manganese. Cool to ambient temperature and transfer to a suitable container ready to carry out step I8.3.

I12.1.4 Alternative Procedure

Immediately after collection pass the sample (not less than 500 ml through a 0.45 μm membrane filter (which has been washed by soaking in 0.1 N nitric acid and rinsing in redistilled water) using a polycarbonate pressure filtration apparatus and a nitrogen pressure of about 0.3 bar. Acidify 100 ml of the filtered water sample to pH 2.8±0.2 by addition of 100±5 μl of 50% (v/v) hydrochloric acid. Irradiate the acidified sample for 2–3 hours in a clean silica tube. Store the irradiated sample in a clean PTFE or fused silica container until analysed.

I12.2 Peroxodisulphate Oxidation

I12.2.1 Reagents

I12.2.1.1 Nitric acid (d_{20} 1.42).

I12.2.1.2 10% V/V Nitric Acid.

Dilute 10±1 ml of nitric acid (d_{20} 1.42) with with water to 100 ml.

I12.2.1.3 25% m/V Ammonoum Peroxodisulphate Solution.

Dissolve 250±1 g of ammonium peroxodisulphate in water and dilute with water to 1 litre. This solution is stable for at least three months.

I12.2.1.4 Aluminium Oxide Anti Bumping Granules.

The aluminium oxide granules should be boiled in 100 ml of 10% V/V nitric acid containing 4 ml of 25% m/V ammonium peroxodisulphate for 1 hour, washed thoroughly with water, dried at 105°C and stored in a clean container.

I12.2.1.5 3% m/m Hydrogen Peroxide (10 volume).

Dilute to 10.0±0.1 ml of 30% m/m hydrogen peroxide (100 volume) with water to 100 ml. This reagent should be freshly prepared each week.

I12.2.1.6 2 M Ammonium Hydroxide (approximately).

Dilute 250±5 ml of isothermally distilled ammonium hydroxide (d_{20} 0.94) (or 8.5 M, see Introduction 6.2.2), with water to 1 litre. This solution is stable for at least three months if stored in a stoppered bottle.

I12.2.2 Oxidation Pretreatment Procedure using Peroxodisulphate

Step	Procedure	Notes
I12.2.2.1	For a flame AAS finish it is necessary to oxidize 100 ml of sample; but for an electrothermal atomization ASS finish smaller volumes are sufficient.	(a) Great care must be taken during these steps to minimize contamination.

Step	Procedure	Notes
	Place up to 1000±10 ml of filtered sample in a suitable sized conical flask. (note a).	
I12.2.2.2	To each 1000 ml of filtered sample add 1.00±0.05 ml of nitric acid (d_{20} 1.42) (note b), 2.0±0.1 ml of 25% m/V ammonium peroxodisulphate and 4–6 aluminium oxide anti-bumping granules. Cover the flask, with a clock glass and heat to boiling on a hot plate. Boil for 5±1 minutes, remove from the hot plate and allow to cool.	(b) If acid has been added during step, I11.3.4 further addition is not necessary.
I12.2.2.3	Add 1.0±0.1 ml of 3% m/V hydrogen peroxide solution to ensure that any precipitated manganese is dissolved.	
I12.2.2.4	Proceed immediately to step I8.3. At steps I8.3.2 and I8.3.3 (note i)	(i) Great care must be taken to avoid over-shooting while adjusting the pH, because the addition of further acid or ammonium hydroxide may invalidate the blank determinations.

J Semi-Micro Determination of Dissolved Cadmium, Copper, Lead and Nickel in Filtered Saline Waters

J1 Performance characteristics of the method

J1.1	Substances determined	Dissolved (passing a 0.45 μm filter) forms of nickel, lead, copper, and cadmium.
J1.2	Type of Sample	Estuarine waters.
J1.3	Basis of Method	Chelation of the dissolved metals with ammonium pyrrolidine dithiocarbamate, extraction into 1,1,1 trichloroethane and instrumental analysis by atomic absorption spectrophotometry. (50).
J1.4	Range of Application	Cadmium 0 to 1.0 μg/l Copper 0 to 10 μg/l Lead 0 to 10 μg/l Nickel 0 to 10 μg/l
J1.5	Calibration curve	linear at least to the top of the range of application. (see J1.4)

J1.6 Total standard deviation

Sample	Found μg/l	s_t μg/l	Degrees of Freedom
Cadmium			
Deionized Water (DW)	0.000	0.005	13
DW + 0.75 μg/l	0.745	0.039	10
Sea Water (SW)	0.035	0.008	9
SW + 0.25 μg/l	0.279	0.018	13
SW + 0.50 μg/l	0.533	0.029	12
SW + 0.75 μg/l	0.754	0.054	13
Copper			
DW	−0.10	0.024	13
DW + 8 μg/l	7.83	0.53	6
SW	1.64	0.11	13
SW + 2 μg/l	3.71	0.19	13
SW + 8 μg/l	9.22	0.51	6
Lead			
DW	0.02	0.16	11
DW + 8 μg/l	7.95	0.41	6
SW	0.25	0.17	4
SW + 2 μg/l	2.61	0.13	12
SW + 8 μg/l	8.19	0.32	11
Nickel			
DW	0.00	0.11	11
DW + 8 μg/l	7.89	0.45	13
SW	0.70	0.09	12
SW + 2 μg/l	2.82	0.17	8
SW + 8 μg/l	8.52	0.41	13

J1.7	Limits of Detection (degrees of freedom in brackets)	(using the within-batch standard deviation of results for acidified deionized water) Cadmium 0.020 μg/l (10) Copper 0.33 μg/l (8) Lead 0.71 μg/l (10) Nickel 0.50 μg/l (10)
J1.8	Sensitivity	(for AAS instrumental settings see Section J6.1) 100 pg Cd = 0.535 absorbance 1,000 pg Cu = 0.380 absorbance 2,000 pg Pb = 0.231 absorbance 2,000 pg Ni = 0.130 absorbance
J1.9	Bias	A small positive bias has been observed for lead at low concentrations—see Section J1.6 for details of recovery tests.
J1.10	Inteferences	There are no known interferences arising from the bulk constituents of saline waters. Carry-over of the saline matrix into the furnace must be avoided, as the major ion constituents of saline waters would then cause interference effects. In common with large scale extraction methods, problems may occur when analysing samples that contain high concentrations of extractable elements, eg Fe, Cu, Pb, Cd, Ni. If such samples are encountered, then it is recommended that spiking recovery experiments are performed to check for the presence of interferences. Some forms of organic matter may cause poor extraction if oxidative pretreatment is not applied (see Sections I3, I8.2 and I12).
J1.1.1	Time required for analysis	A batch of 25 samples is analysed in eight hours, of which 3.5 hours is operator time. Time taken for pre-treatment steps eg ozonolysis or UV photolysis is not included.

J2 Principle

The four metals are complexed as their pyrrolidine dithiocarbamates and extracted into a small volume of 1.1.1 trichloroethane in which these complexes are very soluble, thus achieving a concentration as well as salt removal. The organic solution is then analysed directly by electrothermal atomization AAS.

J3 Interferences

Similar to I3, which see.

J4 Hazards

Similar to I4, which see.

J5 Reagents and Standards

J5.1 Reagent quality

Unless otherwise stated, reagents are Analytical Reagent grade.

J5.2 Water

Deionized or redistilled water should be used for preparing standard and reagent solutions. The trace metal content of this water should be negligible compared with the lowest concentration to be determined in the samples. The metal content of the water should be checked by direct analysis using Electrothermal Atomization AAS.

J5.3 Neutralizing/Chelating Reagent

Dissolve 0.40 ± 0.01 g ammonium pyrrolidine dithiocarbamate (APDC) and 5.00 ± 0.01 g sodium hydrogen carbonate in water and make up to a final volume of 100.0 ± 0.2 ml. In order to purify this reagent, transfer it to a pre-cleaned glass or PTFE container with stopper, add 20 ml 1,1,1-trichloroethane (J5.4) and shake for 5 minutes. Allow the phases to separate before use. When using this reagent care must be taken to pipette only from the upper aqueous layer. If contamination of the reagent during use is suspected, the bottle should be shaken for a further 5 minutes.

J5.4 1,1,1-trichloroethane

1.1,1-trichloroethane may be stored in a refrigerator prior to use, as chilling of the solvent improves pipetting behaviour. Metal levels were generally found to be low in this solvent although, if necessary, it can be purified by redistillation (preferably sub-boiling) (59).

J5.5 Other Reagents and Solutions

J5.5.1 Detergent Solution for cleaning apparatus (Decon 90 or similar) at 5% (v/v) concentration.

J5.5.2 Dilute Nitric Acid (1+9) and (1+1) diluted solutions are also used for cleaning purposes.

J5.5.3 Hydrochloric Acid (d_{20} 1.18) for sample preservation.

J5.6 Standard Solutions

Standard solutions are prepared daily from commercially available 1,000 mg/l AAS standards. Alternatively, stock standard solutions may be prepared from high purity metals (60).

J5.6.1 Solution X (1,000 μg Cd/1)

To a 1,000 ml volumetric flask containing 500 ml (± 300 ml) water, add 1,000 ± ul 1,000 mg Cd/l stock standard solution. Dilute to the mark with water and mix well.

J5.6.2 Solution Y (10,000 μg Pb/l, 10,000 μg Cu/l, 10,000 μg Ni/l)

To a 100 ml volumetric flask containing 50 ± 30 ml water, add the following:

1,000 ± 2 μl of 1,000 mg Cu/l stock standard solution
1,000 ± 2 μl of 1,000 mg Ni/l stock standard solution
1,000 ± 2 μl of 1,000 mg Pb/l stock standard solution

Dilute to the mark with water and mix well.

The following solutions are used as calibrating standards:

J5.6.3 Blank

To a 1,000 ml volumetric flask containing 500 ± 300 ml of water add 5.00 ± 0.05 ml concentrated hydrochloric acid. Dilute to the mark with water and mix well.

J5.6.4 Solution A (2.5 μg Pb/l, 2.5 μg Cu/l, 2.5 μg Ni/l, 0.25 μg Cd/l)
To a 1,000 ml volumetric flask containing 500 ± 300 ml water add:

5 ml ± 0.05 ml of concentrated hydrochloric acid,
250 ± 1 μl of Solution X and
250 ± 1 μl of Solution Y

Dilute to the mark with water and mix well.

J5.6.5 Solution B (5.0 μg Pb/l, 5.0 μg Cu/l, 5.0 μg Ni/l, 0.5 μg Cd/l)
To a 1,000 ml volumetric flask containing 500 ± 300 ml water add:

5 ml ± 0.05 ml of concentrated hydrochloric acid,
500 ± 2 μl of Solution X and
500 ± 2 μl of Solution Y

Dilute to the mark with water and mix well.

J5.5.6 Solution C (7.5 μg Pb/l, 7.5 μg Cu/l, 7.5 μg Ni/l, 0.75 μg Cd/l)
To a 1,000 ml volumetric flask containing 500 ± 300 ml water add:

1,000 ± 2 μl of concentrated hydrochloric acid,
750 ± 2 μl of Solution X and
750 ± 2 μl of Solution Y

Dilute to the mark with water and mix well.

J5.6.7 Solution D (10.0 μg Pb/l, 10.0 μg Cu/l, 10.5 μg Ni/l, 1.0 μg Cd/l)
To a 1,000 ml volumetric flask containing 500 ± 300 ml water add:

5.00 ± 0.01 ml of concentrated hydrochloric acid
1,000 ± 2 μl of Solution X and
1,000 ± 2 μl of Solution Y

Dilute to the mark with water and mix well.

J6 Apparatus

J6.1 Atomic Absorption Spectrophotometer

Any commercially available atomic absorption spectrophotometer suitably equipped with a graphite furnace atomizer, an adjustable autosampler, background correction and preferably a printer is suitable. Instrumental settings should be those given in the manufacturer's instructions. The graphite furnace programmes used to obtain the test data were as follows. Different equipment may require slight variations. Users should ascertain optimum settings for their own equipment.

	Cd	Cu	Pb	Ni
Wavelength nm	228.8	324.7	283.3	232.0
Bandpass nm	0.7	0.7	0.7	0.2
Furnance Dry temp C	110	110	110	110
Ash temp C	250	900	700	900
Atomic Absorption temp C	1,750	2,200	1,750	2,200
Clean Out temp C	2,700	2,700	2,700	2,700
Inject Vol μl	20	20	40	40

Non pyrolytically coated furnace tube.
Stop flow used during atomization.

J6.2 Chemical Work Station

It is advised that sample manipulation and extraction be carried out in a clean air Chemical Work Station. The cabinet combines vertical downflow clean air conditions with fume extraction. This represents the ideal conditions for work, providing minimal risk of contamination from airborne particulates whilst ensuring operator safety.

J6.3 Chemical Apparatus

Polyethylene or PTFE containers should be used for storage of samples and reagents. Sample bottles should have a volume of at least 50 ml. The bottles should have tightly fitting caps made of the same material as the rest of the bottle and containing no insert. Bottles should be first cleaned by washing with detergent solution, thoroughly rinsed with water and then soaked in dilute nitric acid (10% v/v) for at least 48 hours. Bottles should then be washed with copious quantities of pure water before use.

Sample extraction is carried out in 5 ml capacity, leakproof screw cap PFA Teflon conical vials (Cole-Parmer Cat. No. T-8936-29, or similar). For initial cleaning of these, the following procedure is recommended: soak vials and caps in detergent solution for 24 hours, rinse thoroughly with deionized water and soak in hydrochloric acid solution for at least 24 hours, rinse thoroughly with deionized water, soak in 2% (w/v) APDC solution, rinse, and wash finally in 1,1,1 trichloroethane. Once in routine use vials are stored between batches of analyses in (1 + 1) nitric acid and simply rinsed thoroughly with deionized water prior to subsequent use.

J7 Sample Preservation

Samples for trace metals determination should be filtered through a 0.45 μm membrane filter and preserved by addition of 5.00 ± 0.01 ml per litre of concentrated hydrochloric acid (d_{20} 1.18).

J8 Sample Pretreatment

If necessary, the organic content of the sample may be destroyed before analysis by ozonolysis or preferably by UV-photooxidation. Details of these methods may be found in Refs 35, 36 and 61, also see Method I. If pre-treatment steps are employed, then at least one blank and control standard should be put through these stages.

J9 Analytical Procedure

Step	Procedure	Notes
J9.1	**Batch structure.** (This is dependent on the equipment used.) If an autosampler with 35 sample cups on the tray is used a typical batch would consist of 25 samples (including an AQC standard) plus 4 standards and a blank at the beginning and 4 standards and a blank at the end of the run. Repeat analyses of samples are recommended. (See Section J5.6 and J9.3 for details of standards and blanks.)	
J9.2	**Sample extraction**	
J9.2.1	Pipette 2.50 ± 0.01 ml of sample into the extraction vial (note a).	(a) The use of good quality dispensing micropipettes that have been recently calibrated is recommended for those steps.
J9.2.2	Add 250 ± 2 µl of Reagent J5.3 (notes a and b).	
J9.2.3	Add 500 ± 2 µl of 1,1,1-trichloroethane (note a).	(b) For samples where the acidity is unknown, or where the acid addition has been performed inaccurately, the amount of neutralizing solution to be added is determined on a separate sample aliquot and the extra amount of neutralizing solution added is adjusted accordingly.
J9.2.4	Place caps on all cups.	
J9.2.6	Secure the vials in a shaking rig (note c).	(c) The Cole-Parmer vials described in Sections J6.3 are provided in plastic trays in which they can be conveniently secured for manual shaking. If other vials are used a suitable rig will have to be devised.
J9.2.6	Shake rig vigorously for 10 ± 1 minutes (note d).	(d) Although manual shaking has been employed, the use of a mechanical shaker is recommended for this step. However, it is strongly advised that shaking time is optimized for the type of shaker used.
J9.2.7	Allow samples to stand for 5 minutes to allow phases to separate.	
J9.2.8	Remove the caps from extraction vials and, using a dispensing micropetter, transfer the lower 1 ml of solution to the auto-sampler cup (note e).	(e) It is important also to transfer some of the upper aqueous layer along with the 0.5 ml of organic extract in order to prevent evaporation losses.
J9.3	**Atomic Absorption Measurement**	
J9.3.1	Load autosampler tray and start AAS analysis according to the manufacturer's instructions, ensuring that the sampling probe is adjusted to sample from the lower organic layer only (notes f and g). Wavelengths and typical conditions are given in Section J6.1.	(f) Prior to the commencement of analysis, new furnace tubes are conditioned by repeated analysis of extracted mid-range standards until a reproducible signal is obtained (ca 3% relative standard deviation). Conditioning is usually complete within 10 injections. Furnance tubes are replaced after approximately 150 firings.

Step	Procedure	Notes
		(g) Do not aspirate any aqueous layer during the course of a batch of analyses as this can reduce the accuracy with which the organic solvent is pipetted.
J9.3.2	Blanks, standards and AQC samples must be carried through the whole procedure, including extraction. See Section J9.1 for details.	

J10 Calculation of Results

J10.1 For each element construct a calibration curve of absorbance versus concentration of standards.
The mean value of the absorbance recorded at the beginning and the end of each run should be plotted. The calibration line should be constrained to pass through the mean blank absorbance value.

J10.2 Use the calibration curve to calculate the concentration of elements in the sample.

J11 Sources of Error

J11.1 Contamination

Owing to the low concentrations of the determinands, contamination presents a potential problem. Working conditions should therefore be critically examined and precautions taken to minimize this risk. For advice on reducing sample contamination see Refs. 51, 52 and 53.

J11.2 Interferences

Carry-over of the saline matrix into the furnance may occur when the organic layer is close to depletion. This effect is characterized by a high background profile during AAS analysis. Such results should be rejected. Care in performing the analysis should avoid this problem.

K Dissolved Chromium in River, Estuarine and Coastal Water by Iron Collection—Electrothermal Atomic Absorption Spectrophotometry

Note: Throughout this method chromium is expressed as the element Cr.

K1 Performance Characteristics of the Method

K1.1 Substance determined

All forms of chromium (see Section L2.2).

K1.2 Types of sample

River, estuarine and coastal waters.

K1.3 Basis of method

Total chromium is determined by coprecipitating with iron (II) hydroxide (56), followed by atmospheric oxidation, dissolution of the precipitate and electrothermal atomic absorption spectrophotometry, chromium (III) is determined in a similar fashion but using iron (III) hydroxide. (54)

K1.4 Range of application (a)

Up to 1.5 μg/l.

K1.5 Calibration curve (a)

Linear to at least 1.5 μg/l.

K1.6 Within batch standard deviation (a)

Added chromium (VI) concentration (ng/l)	Total chromium found (ng/l)	Standard deviation (ng/l)	Degrees of freedom
0	202	14	5
100	317	18	5
250	440	18	5
500	690	18	5
750	917	32	5
1,000	1,186	39	5

These results for total chromium were obtained with Liverpool tap water, spiked with chromium (VI).

Added chromium (VI) concentration (ng/l)	Chromium (III) found (ng/l)	Standard deviation (ng/l)	Degrees of freedom
Chromium (III)			
0	192	7	5
200	388	10	5
400	585	18	5
600	798	23	5
800	987	22	5
Chromium (VI)			
0	192	8	5
200	199	9	5
400	198	10	5
600	201	7	5
800	203	10	5

These results were obtained by chromium (III) method with Mersey estuary water (S = 28 g/kg) which had been spiked with chromium (III) or chromium (VI).

Added chromium (VI) concentration (ng/l)	Total chromium found (ng/l)	Standard deviation (ng/l)	Degrees of freedom
0	21	2	5
40	64	5	5
100	132	5	5
200	223	8	5
400	418	13	5
600	618	18	5
900	931	23	5
1,200	1,218	39	5
1,400	1,410	43	5

These results were obtained for total chromium with Mersey estuary water (S = 18 g/kg) which had been stripped by coprecipitation with iron (II) hydroxide and spiked with chromium (VI).

K1.7 Limit of detection (a) (b)

32 ng/l with 6 degrees freedom. (c)

K1.8 Sensitivity (a) (b)

100 ng/l gave an absorbance of approximately 0.058.

K1.9 Bias (a)

no bias detected.

K1.10 Interferences (a) (b)

See Table 12.

K1.11 Time required for analysis (a)

The total and operator times for the analysis of ten samples are approximately five hours and two-and-a-half hours respectively.

(a) These data were obtained for 250 ml sample volumes in the Oceanography Department, University of Liverpool, using a Perkin Elmer model 2280 atomic absorption spectrophotometer, with a Model HGA400 heated graphite atomizer, and a Model AS1 automatic sampled iftted with a 20 μl syringe. A PRS10 printer sequencer was used as read out. Other similar AAS instruments will be equally suitable.

(b) These characteristics will vary considerably according to the make and type of atomic absorption spectrophotometer and electrothermal atomizer used.

(c) Each measurement was the mean obtained for three separate injections.

K2 Principle

K2.1 The method for dissolved chromium described is based on a procedure developed by Cranston and Murray (55) which has been slightly modified at the Department of Oceanography, University of Liverpool.

K2.2 Procedures are described for the determination of both total dissolved chromium (ie $Cr^{3+} + Cr^{6+}$) and chromium (VI). In the determination of total chromium the filtered sample is treated with a suspension of iron (II) hydroxide; this reduces chromium (VI) to chromium (III). Atmospheric oxidation converts the iron to iron (III) hydroxide which coprecipitates chromium. The precipitate is filtered off and dissolved in hydrochloric acid. Chromium is determined in the solution by electrothermal atomic absorption analysis. Chromium (III) alone is determined in a similar fashion, but replacing iron (II) hydroxide by iron (III) hydroxide.

Table 12

Effect of other elements on the determination of 500 ng/l chromium (VI) (d) (e)

Other element	Other element added as	Conc. other element μ/l	Effect in ng/l Cr of other element (f)
Aluminium	ammonium sulphate	50	+13
Antimony (III)	potassium antimonyl tartrate	50	+13
Cadmium	nitrate	100	−18
Cobalt	nitrate	100	+5
Copper	sulphate	10,000	+9
Lead	nitrate	5,000	−22
Manganese (II)	sulphate	5,000	−19
Mercury (II)	chloride	10	+13
Molybdenum (VI)	ammonium molybdate	1,000	+20
Nickel	sulphate	5,000	−27
Selenium (IV)	sodium selenite	50	+15
Tin (II)	chloride	2,000	−22
Vanadium (V)	ammonium vandate	1,000	−27
Zinc	sulphate	2,000	−22

(d) Interference studies were made in chromium-stripped sea water (S = 34 g/kg). The results are based on differences between chromium spiked and unspiked samples, as the compounds used, although of analytical reagent grade, contained enough chromium to cause significant absorbances with the unspiked samples.

(e) The major cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}) and anions (Cl^-, SO_4^{2-}, Br^-) cause no interferences at their concentrations in sea water of salinity 35 g/kg.

(f) If the other substance did not interfere the effect would be expected (95% confidence) to lie within the range 500 ± 40 μg/l.

K2.3 Samples in which chromium (III) is to be determined should be filtered and analysed without acidification within one to two hours of collection in order to avoid changes in the oxidation state.

K2.4 For most types of sample, pretreatment is not usually necessary. Experience, however, will show when it is required, and, if it is applied, it is only valid when total chromium is to be determined.

K3 Interferences

The effect of other substances on the determination of total chromium by the method described is shown in Table 12. The data were obtained by the Department of Oceanography, University of Liverpool using the instrumentation listed in the footnote (a) of Section L1. The effects may be different with other instruments.

K4 Hazards

Care must be taken to avoid exposure to the intense ultra-violet radiation produced by the mercury lamp because this can cause permanent eye and skin damage. The photolysis apparatus produces copious amounts of ozone which is toxic and it is essential that the cooling air is vented to a fume hood.

K5 Reagents

Only ultra-pure grades of reagents are suitable for the analysis and, even with these, each new batch should be checked for purity by 'blank' determinations. Reagent solutions and suspensions should be stored in polyethylene bottles which have been cleaned by soaking overnight in 10% v/v hydrochloric acid and washing copiously with water.

K5.1 Water

The water used for the blank determinations and for preparing standard and reagent solutions should have a chromium content that is negligible compared with the lowest concentration to be determined in the samples. Water redistilled from an all-glass or all-silica apparatus is normally suitable.

K5.2 Hydrochloric acid (d_{20} 1.18)

K5.3 10% v/v Hydrochloric Acid

This solution, which is used for cleaning apparatus, can be prepared by 1:10 v/v dilution of analytical reagent grade hydrochloric acid (d_{20} 1.18).

K5.4 10% Ammonia Solution

Dilute 50 ± 2 ml of ultrapure ammonia solution (d_{20}, 0.880) with water to 500 ml in a calibrated flask.

K5.5 Sulphuric Acid (d_{20} 1.84)

K5.6 10% Ammonium Iron (II) Sulphate

A grade containing less than 1 μg/g chromium must be used. A spectrographically standardized grade of chemical has been found to be suitable.

K5.7 Iron (II) Hydroxide Suspension

Weigh 0.60 ± 0.05 g of ammonium iron (II) sulphate into a 100 ml conical flask. Add 50 ± 2 ml of water which has been acidified with one drop (ca. 0.03 ml) of concentrated sulphuric acid and stir until the solid has dissolved. Then, while stirring, add 3.0 ± 0.1 ml of 10% ammonia solution (K5.4). The resultant suspension must be used within ten minutes of preparation.

K5.8 Iron (III) Hydroxide Suspension

Allow iron (II) hydroxide suspension, prepared as described in Section L5.7, to stand for 24 hours. Check that the final pH lies between 8 and 9 and if necessary cautiously add 10% ammonia solution to bring it into this range. This suspension should be prepared monthly.

K5.9 Standard Chromium Solutions

K5.9.1 Chromium (III)

K5.9.1.1 Solution A: 1 ml contains 100 μg chromium (III)
Dissolve 0.960 ± 0.002 g of chromium (III) potassium sulphate in about 200 ml of water containing 2.0 ± 0.1 ml of hydrochloric acid (d_{20} 1.18). Dilute with water to 1 litre in a calibrated flask. This solution is stable for at least three months.

K5.9.1.2 Solution B: 1 ml contains 1 μg chromium (III)
Dilute 10.00 ± 0.05 ml of Solution A with water to 1 litre in a calibrated flask containing 1.0 ± 0.1 ml of hydrochloric acid (d_{20} 1.18). This solution should be freshly prepared before use.

K5.9.1.3 Solution C: 1 ml contains 25 ng chromium (III)
Dilute 2.500 ± 0.005 ml of Solution B with water to 1 litre in a calibrated flask. This solution should be prepared freshly before use.

K5.9.2 Chromium (VI)

K5.9.2.1 Solution D: 1 ml contains 100 μg chromium (VI)
Dissolve 0.2828 ± 0.0002 g of potassium dichromate, dried at 105°C for one hour, in about 500 ml of water containing 2.0 ± 0.01 ml of hydrochloric acid (d_{20} 1.18), and dilute with water to 1 litre in a calibrated flask. This solution is stable for at least three months.

K5.9.2.2 Solution E: 1 ml contains 1 μg chromium (VI)
Dilute 10.0 ± 0.05 ml of Solution A with water to 1 litre in a calibrated flask containing 1.0 ± 0.1 ml of hydrochloric acid. This solution should be prepared freshly before use.

K5.9.2.3 Solution F: 1 ml contains 1 μg chromium (VI)
Dilute 2.500 ± 0.005 ml of Solution B with water to 1 litre in a calibrated flask. This solution should be prepared freshly before use.

K6 Apparatus

K6.1 Glassware

If possible, apparatus should be reserved solely for chromium determinations. Clean all glass and polythylene ware by soaking it in 10% v/v hydrochloric acid overnight. Rinse thoroughly with water.

K6.2 Filtration Apparatus

K6.2.1 For filtration of samples

Filtration of samples to remove particulate matter is carried out using the apparatus shown diagrammatically in Fig 29. It consists of a 500 ml plastic separating funnel fitted with a PTFE stopcock. This is connected to a 47 mm in-line filter (Millipore Swinnex filter, Catalogue No. SXHA 047 OS is suitable) by means of silicone tubing. Flow of sample is induced by the application to the top of the funnel of a pressure of approximately 1 bar of filtered nitrogen from a cylinder fitted with a pressure regulator. Filtration is carried out using a 47 mm diameter membrane filter of pore size 0.45 um (Millipore HA filters have been found to have satisfactory filtration characteristics).

K6.6.2 For filtration of hydroxide precipitates

Filtration of the hydroxide precipitates is carried out using a 25 mm membrane filter mounted over a sintered disc held in a perspex filter holder (Fig 30). The holder is fitted to a 500 ml filter flask which is evacuated using a filter pump. The membrane filter should have a pore size of approximately 0.4 um, be insoluble in concentrated hydrochloric acid and have a chromium content of <20 ng per filter. Comparatively few makes of filters meet the last two of these criteria, but Nuclepore No. 110607 polycarbonate filters have been found to be satisfactory (55.56).

K6.3 Screw-topped Polypropylene Bottles (250 ml)

K6.4 30 ml Polystyrene Containers fitted with polypropylene closures (Sterilin 128A tubes are suitable).

K6.5 Atomic Absorption Spectrophotometer

An atomic absorption spectrophotometer with a hollow cathode chromium lamp and fitted with an electrothermal atomizer and automatic sample injector is employed. The graphite tubes must be pyrolytically coated and argon must be used as purge gas. Automatic background correction should be used. The optimum settings of the programmer of the electrothermal atomizer will vary from one instrument to another. They must be found experimentally using the manufacturer's recommendations as a guide. (See also ref 21 on the use of a nitrous oxide-acetylene flame.)

K6.6 Ultra-violet Photolysis Apparatus

The apparatus which is used for pretreatment of water samples (section L8.1) is shown diagrammatically in Fig 28. It consists of a cylindrical aluminium box containing an axially mounted 1 kW medium pressure mercury lamp around which are arranged ten 25 cm by 4 cm diameter fused silica photolysis tubes, each at a distance of 10 cm from the lamp. Cooling to the optimum temperature of 60°C ± 3°C is achieved by an externally mounted fan which draws air through the lamp chamber and expels it to a fume cupboard to vent ozone. The lid of the photolysis apparatus is fitted with an interlocked micro-switch which prevents the mercury lamp being used when the lid is open.

K7 Sample Collection and Preservation

Samples containing appreciable amounts of suspended matter must be filtered through a tared membrane filter using the apparatus described in Section K6.2.1, within two to three hours of collection. Before carrying out the filtration, wash the filter with 100 ml of 10% v/v hydrochloric acid (Section K5.3) followed by 100 ml of water. The filter can be subsequently washed with 2×10 ml of water, dried at 60°C on a watch

glass, weighed and then retained in a polypropylene specimen tube for the determination of particulate chromium (see Method L). Because of the risk of changes occurring in the oxidation state of chromium, it is essential to commence analyses for chromium (III) immediately. If total dissolved chromium is to be determined, it is desirable to carry out the first stage of the analysis (K8.2.1) before storage. However, if this is not possible, samples can be stored unchanged for several weeks if acidified to pH2 with hydrochloric acid. It is not possible to preserve samples which are to be analysed for chromium (III) in this way.

K8 Analytical Procedure

Read section K4 on hazards before starting this procedure.

A pretreatment procedure is described followed by methods for the determination of total chromium and chromium (III)

Step	Procedure	Notes
K8.1	Pretreatment (notes and b)	(a) If pretreatment is not required, start at K8.2.1. (b) The pretreatment stage cannot be used if chromium (III) is to be determined alone.
K8.1.1	Transfer 250 ± 2 ml of the sample to a silica photolysis tube; if necessary, cautiously adjust the pH to 8.0 ± 0.3 using a meter, by addition of hydrochloric acid or ammonia solution as appropriate.	
K8.1.2	Loosely close the tube with a bulb stopper and place it in the photolysis apparatus.	
K8.1.3	Irradiate the sample for two to three hours (note c) and then cool to ambient temperature.	(c) The temperature of the solution should not exceed 70°C.
K8.1.4	Quantitatively transfer the liquid to a 250 ml polypropylene bottle, using 2 ml portions of water to rinse the tube. Proceed to K8.2.2.	
K8.1.5	Carry out a blank by performing steps K8.1.1 to K8.1.4 using 250 ml of water instead of the sample.	
K8.2	Determination of total chromium	
K8.2.1	Place 250 ± 2 ml of the filtered sample in a 250 ml polypropylene bottle (see note d).	(d) This volume is suitable for chromium concentrations of up to 1.5 μg/l. For higher concentrations the volume taken should be reduced according to the expected concentration of chromium, and water should be added to give a total volume of 250 ± 2 ml.
K8.2.2	If necessary, using a glass electrode, adjust the pH value of the sample to 8.0 ± 0.3 by dropwise addition of ammonia solution or hydrochloric acid, as appropriate.	
K8.2.3	By means of a pipette add 1.0 ml of iron (II) hydroxide suspension, stopper the bottle tightly, and shake for one hour on a mechanical shaker.	
K8.2.4	Allow the precipitate to settle overnight and decant the supernatant liquid through a 0.45 μm membrane filter held in the filter holder shown in	

Step	Procedure	Notes
	Fig 30. Transfer the precipitate to the filter quantitatively using a jet of water to wash down the sides and shoulder of the apparatus to ensure that all the precipitate is transferred to the filter.	
K8.2.5	Remove the filter from the holder, transfer it to a dry 30 ml polystyrene tube (Section K6.4) and stopper tightly (see note e).	(e) Filters can be stored for several weeks at this stage.
K8.2.6	Treat the precipitate with 0.50 ± 0.02 ml of hydrochloric acid (d_{20} 1.18) and allow to digest for one to two minutes. Then add 9.50 ± 0.05 ml of water using an automatic pipette. Stopper the tube and mix well.	
K8.2.7	Proceed to the atomic absorption stage, K8.3.	
	Blank determination	
K8.2.8	A blank (see K8.1.5) must be run with each batch of determinations using the same batches of reagents that were used for the analysis of the samples. If the samples were filtered before analysis, filter a similar volume of water through a membrane filter as described in Section K7 (note f). Transfer 250 ± 2 ml of the filtrate to a polypropylene bottle and carry out steps K8.2.1 K8.2.7 inclusive. The membrane filter should be retained and used in the blank determination for particulate chromium (L.7.8).	(f) If the samples were not filtered this filtration step should be omitted and 250 ± 2 ml of the water transferred directly to a polypropylene bottle before carrying out steps K8.2.1 to K8.2.7 inclusive.
	Calibration standards	
K8.2.9	Duplicate calibration standards and a corresponding blank must be run with each batch of determinations using the same batches of reagents that were used for the samples. To each of three 250 ml polypropylene bottles add 240 ± 2 ml of water, and to two of them add from a pipette, 10.0 ml of standard chromium (III) Solution C. This corresponds to a chromium concentration of 1.0 μg/l.	
K8.2.10	Carry out steps K8.2.1 to K8.2.7 inclusive.	

K8.3 Atomic absorption stage

K8.3.1 Set up the atomic absorption spectrophotometer according to the manufacturer's instructions. Adjust the wavelength to 357.9 nm and set the programmer of the electrothermal atomizer to the appropriate values.

The following settings were used to obtain the test data. Different equipment may require slight variations. Users should ascertain this optimum setting for their equipment

Drying step	
Ramp time	10 seconds
Temperature	110°C
Hold time	25 seconds

Step	Procedure	Notes
	Pyrolysis step Ramp time 20 seconds Temperature 1,200°C Hold time 5 seconds Atomization step Ramp time 1 second Temperature 2,630°C Hold time 2 seconds Cleaning step Ramp time 1 second Temperature 2,700°C Hold time 2 seconds	
K8.3.2	Transfer the solutions of the precipitates to the sample cups. Carry out three separate injections of 20 µl of each solution into the graphite tube furnace. Run each calibration standard and the corresponding blank both before and after the batch of samples.	
K8.4	**Calculation of results** Calculate the concentration A of chromium in the sample (note g). $A = \frac{S-B}{C-B'}$ µg/l $C = \frac{C_1+C_2+C_3+C_4}{4}$ $B' = \frac{B'_1+B'_2}{2}$ Where S is the mean response for the triplicate injections of the sample concentrate; B is the mean response for the triplicate injection of the blank; C_1, C_2, C_3 and C_4 are the mean responses given by triplicate injections of the concentrates from the 1.0 µg/l standards; B'_1 and B'_2 are the mean responses given by triplicate injections of the blank run with the standards before and after each batch (K8.2.8 and K8.2.9). This calculation assumes a linear calibration curve.	(g) This calculation assumes a sample volume of 250 ml was used.

K9 Checking the Linearity of the Calibration Curve

The procedure described 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 a series of 250 ml polypropylene bottles add, using a pipette, 2.50 ml, 5.00 ml, 10.00 ml and 15.00 ml of standard chromium (VI) Solution F, and dilute to 250 ± 2 ml with water. These solutions correspond to chromium concentrations of 0.25, 0.50, 1.00 and 1.50 µg/l respectively. Carry out steps K8.1 to K8.2.7 and K8.3 inclusive. Also perform a blank as described in K8.1.5, K8.2.8 and K8.3.1 to K8.3.2. Plot the mean response for each sample against µg/l chromium after deduction of the blank.

The calibration curve is normally linear to 1.5 μg/l chromium; however, the linear range of the instrument must be checked. If the curve departs from linearity, sample volumes should be changed so that they give responses which lie on the linear part of the curve.

K10 Change of Concentration Range of the Method

If the chromium content of the sample is likely to exceed 1.5 μg/l chromium; however, the linear range of the instrument will depend on the type of instrument used and therefore linearity must be checked. If the curve departs from linearity sample volumes should be changed so that they give responses which lie on the linear part of the curve.

$$A = \frac{(S-B)}{(C-B)} \times \frac{250}{V} \text{ μg/l chromium}$$

K11 Sources of Error

The following subsections summarize the principal sources of error.

K11.1 Contamination

Because of the very low levels of chromium present in unpolluted natural waters great care must be taken to avoid contamination during sampling, storage, and analysis. It is essential to carry out the analysis in a laboratory in which no appreciable amounts of chromium or its compounds are handled. It is highly desirable to carry out manipulations in a clean laboratory or laminar flow hood. Only reagents of the highest available purity should be used in the analysis and all apparatus used in the analysis should be reserved solely for chromium determinations. Before commencing the analysis of samples, a preliminary series of blank determinations should be run to ensure that the blanks are acceptably low (<40 ng/l chromium).

K11.2 Chromium content of the water used for blank determinations

If the water used for the blank determinations contains a significant concentration of chromium the results will be falsely low. Generally, water doubly distilled from a silica still, or that prepared by deionization of distilled water has been found to give negligible blanks. If high blanks are found, which cannot be attributed to impurities in the reagents, the purity of the water can be checked using the following procedure:

(a) To a 500 ml polypropylene bottle transfer 500 ± 5 ml of the water and treat it as described in steps K8.2.3 to K8.2.7 and K8.4 inclusive. Let the absorbance reading obtained be A_1.

(b) To a similar polypropylene bottle transfer 250 ± 2 ml of water and go through the same steps. Let the absorbance reading be A_2.

(c) The chromium content of the water A_w is then given by

$$A_w = \frac{(A_1 - A_2)}{(C - A_2)} \text{ μg/l}$$

where C is the absorbance reading for a calibration standard carried through the whole procedure (see steps K8.2.9).

K11.3 Interferences

See Section K3. The effect of possible interfering substances may be determined by carrying out determinations on water which has been spiked with known amounts of the substance in the presence of a known amount of chromium as well as in its absence. It should be noted that most analytical grade chemicals contain sufficient chromium to give absorbances significantly greater than the blank when present at concentrations greater than 100 μg of the element concerned per litre. An indication of the extent of possible interference can be obtained from the difference between the absorbance readings obtained with the samples spiked and unspiked with chromium. (If in doubt, purity of reagents should be checked by a completely different method such as X-ray fluorescence on the solid or DC arc or ICP emission spectroscopy as appropriate).

K11.4 Calibration standards

The calibration curve for this method has been found to be linear although its slope may vary from one set of determinations to another, and even, to a lesser extent, during the analysis of a batch of samples. Such variations are caused by changes in the

sensitivity of the atomic absorption spectrophotometer and in the performance of the electrothermal atomizer particularly as the graphite tube ages. It is essential to run the calibration standards and blank both at the beginning and end of each batch of samples.

Figure 28 Ultraviolet photolysis apparatus for pretreatment of water samples

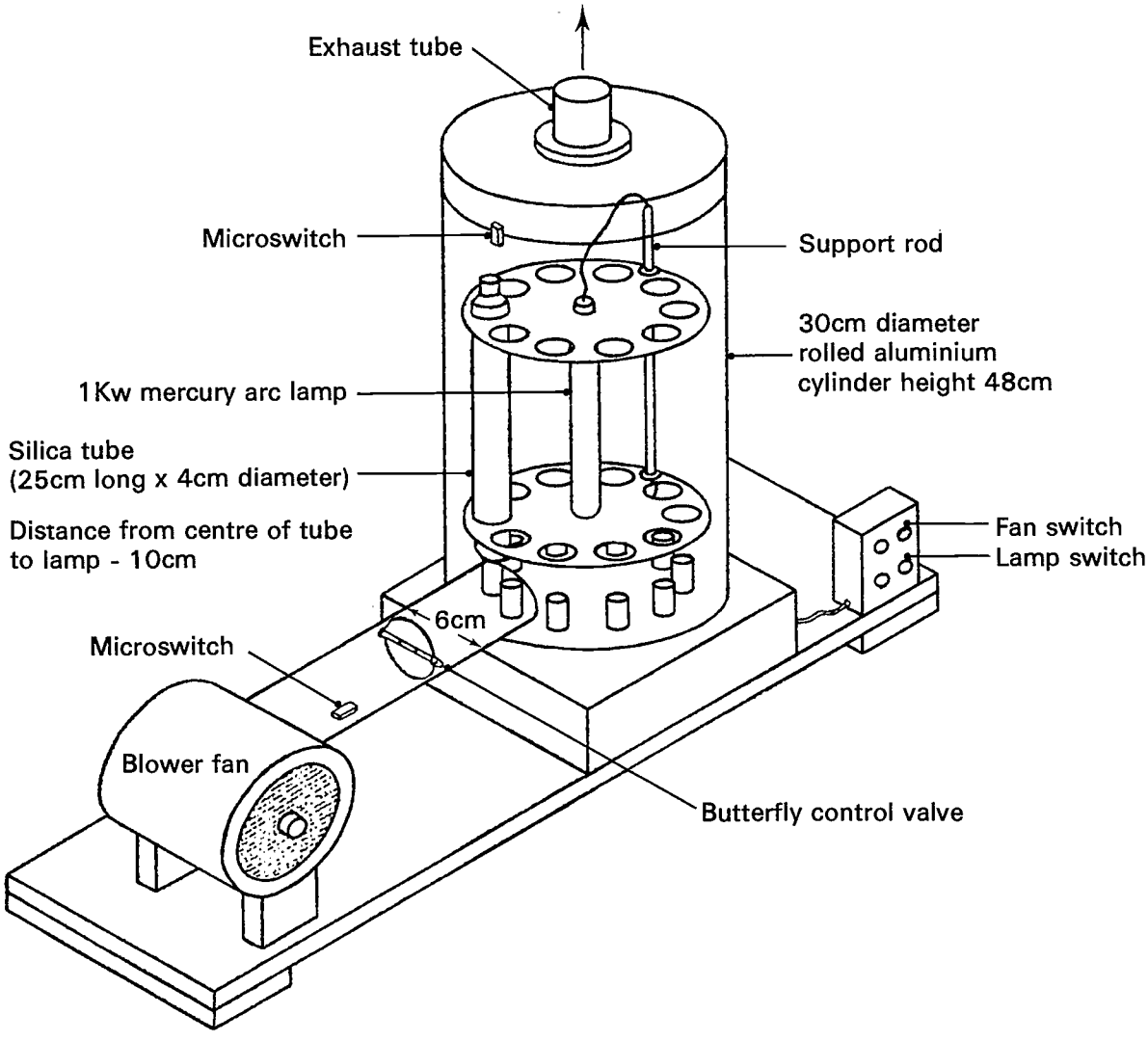


Figure 29 Filtration apparatus for separation of particulate material from sample

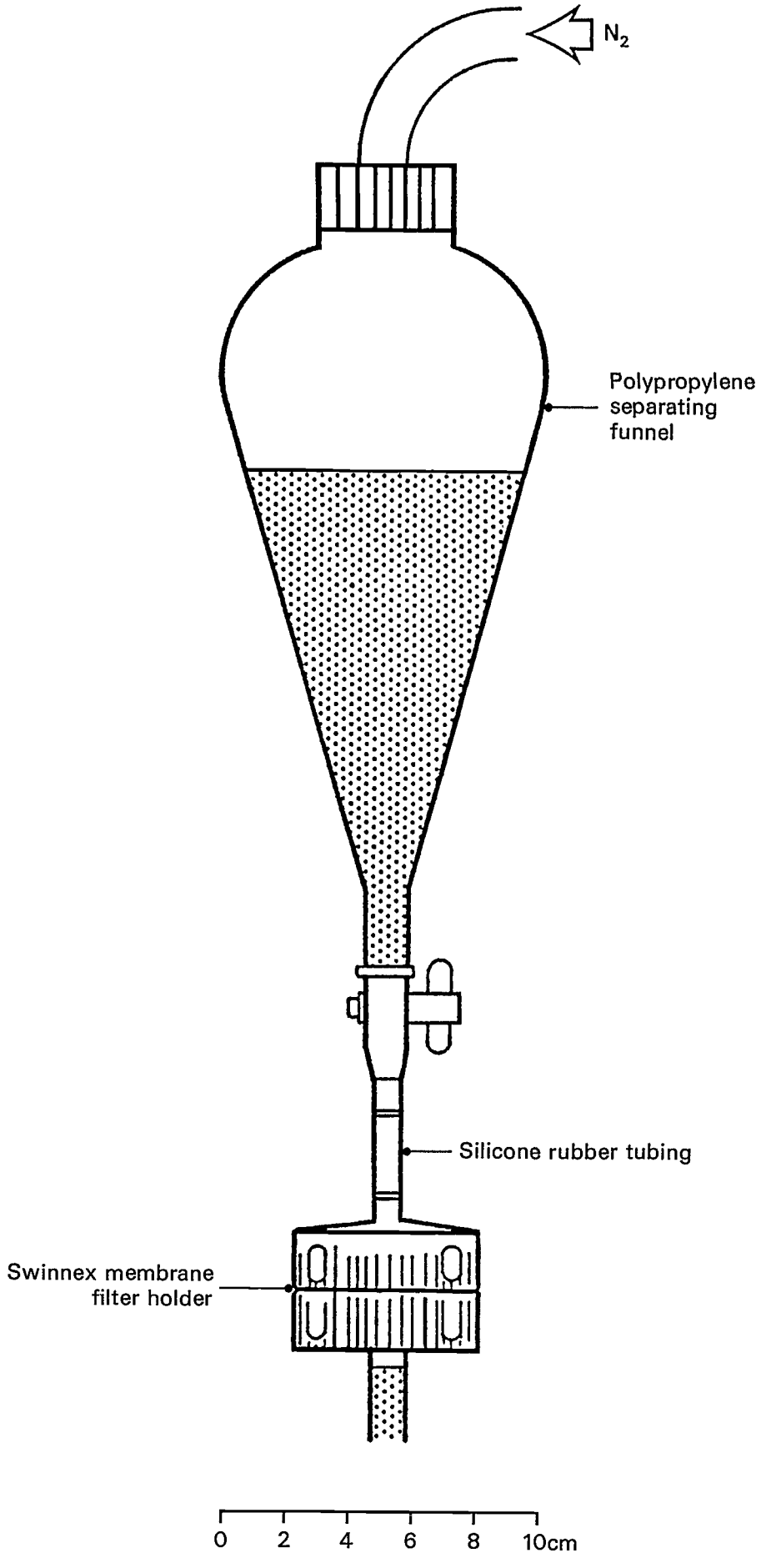
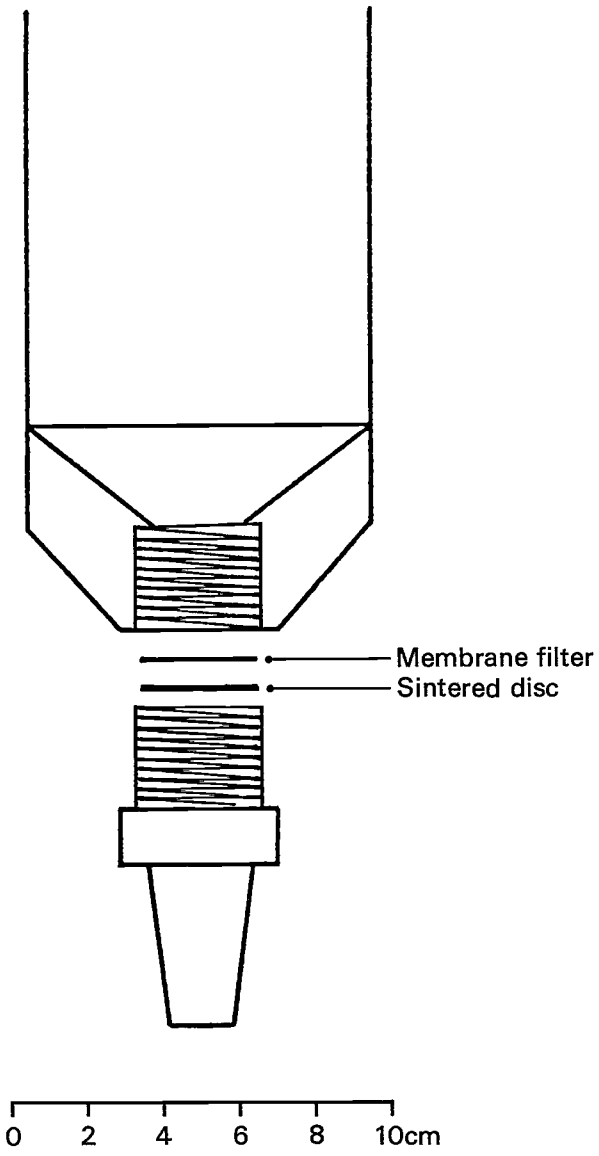


Figure 30 Filtration apparatus for separation of iron (III) hydroxide



L Method for the Determination of Total Particulate Chromium in River, Estuarine and Coastal Waters

L1 Performance Characteristics of the Method

L1.1 Substance determined

Total chromium (a).

L1.2 Type of sample

Particulate material from rivers, estuaries and coastal waters

L1.3 Basis of method

Removal of particulate material by filtration followed by HF/HNO_3 digestion and atomic absorption spectrophotometry (with flame or electrothermal atomization as appropriate). (54).

L1.4 Range of application

Variable dependent on amount of suspended matter filtered.

L1.5 Within batch standard deviation

Mersey mud: concentration 90 μg/g Cr; s.d. 1.7 μg/g (n = 6) (b).

Indiana Harbour Canal NBS Standard Sediment No 1645: concentration 3.04% Cr; s.d. 0.15% (n = 6) (b).

Suspended matter from Mersey estuary:
concentration 162 μg/g Cr; s.d. 10 μg/g (n = 4) (b) (e)
concentration 162 μg/g Cr; s.d. 10 μg/g (n = 4) (c) (e)

L1.6 Interferences (b) (c) (d)

See Table 13.

(a) Certain chromium minerals (eg chromite) are not attacked by the digestion procedure used. However, they are unlikely either to be significant components of the suspended particulates or, because of their insolubility, to be ecologically significant.

(b) These data were obtained in the Department of Oceanography, University of Liverpool, on an Instrument Laboratories atomic absorption spectrophotometer (Model IL 351) using flame atomization (air-C_2H_2).

(c) These data were obtained in the Department of Oceanography, University of Liverpool by electrothermal atomization using the equipment described in footnote (a) of Method L, Section L1.

(d) The performance characteristics are likely to vary considerably according to the make and type of atomic absorption spectrophotometer and electrothermal atomizer used.

(e) Quadruplicate 1-litre aliquots of a well-mixed sample of Mersey estuary water were filtered. The filters and particulates were digested with HF/HNO_3 and analysed by both flame and (after dilution) by electrothermal AAS.

Table 13.

Effect of other substances on determination of chromium by flame (air – C_2H_2) and electrothermal atomization atomic absorption spectrophotometry

		Flame AAS		Electrothermal AAS	
Other Substance	Other substance added as	Conc. of other substance (mg/l)	Effect in μg/ml Cr of other substance at Cr conc. of 2.5 μg/ml*	Conc. of other substance (μg/ml)	Effect in ng/ml Cr of other substance at Cr Conc. of 100 ng/ml†
Aluminium	nitrate	500	−0.04	500	+1
Calcium	chloride	500	+0.10	50	+5
Cobalt	nitrate	10	−0.05	5	± 0
Copper	nitrate	10	−0.02	20	−1
Iron (III)	nitrate	500	+0.08	50	+5
Magnesium	nitrate	200	+0.05	20	−1
Manganese	nitrate	10	−0.03	50	± 0
Nickel	nitrate	5	−0.03	5	−1
Potassium	chloride	200	± 0.00	100	± 0
Sodium	chloride	1000	± 0.00	—	—
Zinc	nitrate	5	−0.02	5	−2
Bromide	potassium salt	10	−0.04	10	−1
Phosphate	di-potassium salt	2.5	+0.03	10	0
Sulphate	sodium salt	100	+0.02	10	0

* If the other substance did not interfere the effect would be expected to lie (95% confidence) between 0.0±0.10 μg/ml at 2.50 μg/ml chromium.
† If the other substance did not interfere the effect would be expected to be (95% confidence) between 0±8 ng/ml at 100 ng/ml chromium.

L1.7 Bias

Not known

L1.8 Time required for analysis

Will depend on ease with which the particular sample dissolves. Typical total and operator times for the analysis of ten samples are approximately ten days and three hours respectively, including filtration.

L2 Principle

The water sample is filtered using a membrane filter. The filter and particulate matter are digested with nitric acid and then with nitric plus hydrofluoric acids until dissolution is complete. The solution is evaporated to dryness three times with nitric acid to remove fluoride and the residue is taken up in dilute nitric acid. Chromium is determined by atomic absorption spectrophotometry using either flame or electrothermal atomization, as appropriate. (See also ref 21).

L3 Interferences

The effect of other substances on the determination of chromium has been measured by the Department of Oceanography, University of Liverpool and is shown in Table 13.

L4 Hazards

Hydrofluoric acid can produce severe skin burns associated with toxic symptoms which may not be noticed immediately due to a local anaesthetic effect hydrofluoric acid sometimes has on skin. Use gloves and eye protection.

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

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

L5 Reagents

L5.1 Water

The water used for blank determinations and for preparing reagents must have a chromium content which is negligible relative to the lowest concentrations to be determined in the samples. Water redistilled from an all glass apparatus is normally suitable. The chromium content of any water suspected of being contaminated can be determined as described in Method K Section K11.2.

L5.2 Nitric Acid

Redistill analytical reagent grade nitric acid (d_{20} 1.42) from a silica still.

L5.3 10% v/v Nitric Acid prepared by quantitative dilution from analytical grade acid (d_{20} 1.42).

L5.4 0.1 M Nitric Acid

Dilute 6.3 ± 0.2 ml of nitric acid (L5.3) to 1 litre with water.

L5.5 40% m/m Hydrofluoric acid (for handling advice see L4 and ref 21)

Ultra-pure hydrofluoric acid must be used.

L5.6 20% m/v Ammonium Chloride Solution

Dissolve 20.0 ± 0.5 g of analytical grade ammonium chloride in water and dilute to 100 ml in a measuring cylinder.

L5.7 Standard Chromium (III) Solutions

Standard chromium (III) solutions as detailed in Method K Section K5.9.1 should be prepared, but using the same volume of nitric acid (d_{20} 1.42) in place of the hydrochloric acid in K5.9.1.1 and K5.9.1.2.

L6 Apparatus

L6.1 Cleaning of glassware and plasticware

All glass and plasticware should be cleaned by soaking overnight in 10% v/v nitric acid (Section L5.3) and then rinsed thoroughly with water.

L6.2 Filtration apparatus see Method K Section K6.2.1.

L6.3 Polytetrafluoroethylene (PTFE) Beakers (50 ml) with covers made of the same material

Before use, clean by heating to boiling with 10 ml of nitric acid (d_{20} 1.42) and then washing well with water.

L6.4 Hotplate

L6.5 30 ml Polystyrene Containers see Method K Section K6.4

L6.6 Atomic Absorption spectrophotometer

As described in Method K Section K6.5; for samples rich in particulate material flame atomization (air C_2H_2) should be used. (See also ref 21 on the use of a nitrous oxide-acetylene flame).

L7 Analytical Procedure

Read Section 4 on hazards before starting this procedure

Step	Procedure	Notes
	Sample	
L7.1	Transfer the weighed filter carrying the particulate material (from Section K7) to a PTFE beaker and rinse out the containing tube into the beaker with a few ml of water.	
L7.2	Evaporate the water on a hot plate at a temperature of about 90°C and add 10.0 ± 0.2 ml of nitric acid (L5.2). Cover the beaker and simmer it on a hot plate for two days at a temperature a few degrees below the boiling point of the acid.	
L7.3	Allow to cool for a few minutes, make up to about 5 ml with nitric acid (d_{20} 1.42) and then add 5.0 ± 0.3 ml of hydrofluoric acid. Cover the beaker and again heat it on the hot plate until all the particulate material has dissolved. (note a).	(a) Up to ten days may be required depending on the composition of the particulate material. (See also ref 21).
L7.4	Remove the cover from the beaker and evaporate almost to dryness (note b). Add 5 ml of nitric acid (section L5.2) and again evaporate almost to dryness (note b). Repeat the evaporation with nitric acid two more times or until the residue will dissolve completely in 0.1 M nitric acid.	(b) Do not bake the residue.

Step	Procedure	Notes
L7.5	Take up the residue in 0.1 M nitric acid (L5.3) and dilute with the same acid to 10 ml in a calibrated flask containing 1 ml of 20% m/v, ammonium chloride solution. (note c)	
L7.6	Transfer the solution to a dry screw-topped polypropylene tube (section L6.4) for storage.	
L7.7	Proceed to the atomic absorption step L7.11 (note c).	(c) Flame atomic absorption should not be used if the particulate loading is low or if the particulate matter is poor in chromium. In such cases omit the addition of ammonium chloride solution and carry out electrothermal atomisation as described in Method K steps K8.3.1 to K8.3.2 but injecting 10 μl and dry at 130°C.
	Blank Determination	
L7.8	Carry out a blank determination as described in steps L7.1 to L7.6 using instead of the filter + particulate matter a similar membrane filter through which 100 ml of water has been filtered.	
L7.9	Proceed to the atomic absorption step L7.11 (note c).	
	Calibration Standards	
L7.10	Duplicate calibration standards must be run with each batch of determinations. Proceed as described in steps L7.8 and L7.9, but adding 0.10 ml of standard chromium III Solution A before the initial nitric acid treatment (note d). This corresponds to 10 μg Cr.	(d) 2.0 ml of standard chromium (III) Solution C should be used if electrothermal nebulization is to be used. This corresponds to 50 ng Cr.
	Atomic Absorption Spectrophotometry	
L7.11	Set up the instrument according to the manufacturer's instructions. Set the wavelength to 357.9 nm. The acetylene flow should be adjusted so that the flame is on the verge of luminosity; only a slight yellow luminosity should be visible. Under these flame conditions interference effects are minimized (see also ref 21).	
L7.12	Aspirate 0.1 M nitric acid and adjust the instrument to read zero. Aspirate one of the calibration standards and adjust the instrument to give a suitable response.	
L7.13	Aspirate 0.1 M nitric acid and read just the zero if necessary. Aspirate both calibration standards with an aspiration of 0.1 M nitric acid between each. Let the responses of the calibration standards be C_1 and C_2.	
L7.14	Aspirate the blank and then the 0.1 M nitric acid. Measure the response of the blank B_1. Aspirate the samples with a wash with 0.1 M nitric acid after each. Measure the instrumental response of each sample S.	

Step	Procedure	Notes
L7.15	To check for any instrumental drift aspirate both calibration standards and the blank with a wash with 0.1 M nitric acid after each and measure the instrumental responses C_3, C_4 and B_2 respectively. If C_1, C_2, C_3 and C_4 and also B_1 and B_2 are in satisfactory accordance, calculate the means $\bar{C}$ and $\bar{B}$.	
	Calculations of results	
L7.16	Calculate the concentration D of chromium in the particulate matter from $D = \frac{10(S - \bar{B})}{(\bar{C} - \bar{B})W} \mu g / g$ where W is the weight of particulate matter. These calculations assume a linear calibration curve. Linearity must be checked.	(e) When electrothermal atomization is used $D = \frac{0.05(S - \bar{B})}{(\bar{C} - \bar{B})W} \mu g / g$

L8 Checking the Linearity of the Calibration Curve

The procedure given in this section must be carried out on at least two independent occasions before this method is applied to any samples and regularly thereafter.

To a series of 100 ml calibrated flasks add, using a pipette, 0.2, 0.5, 1.0, 2.0, 3.0 and 4.0 ml of standard chromium (III) solution B. Dilute to volume with 0.1 M nitric acid. These solutions correspond to chromium concentrations of 0.2, 0.5, 1.0, 2.0, 3.0 and 4.0 mg/l respectively. When electrothermal atomization is employed carry out the above procedure using standard chromium (III) solution B but dilute to 1 litre instead of 100 ml. Carry out steps L7.11 to L7.15 inclusive. Plot the response against μg/l chromium. The calibration curve for flame atomization is normally linear to 3 mg/l chromium and for electrothermal atomization linearity is usually maintained to about 0.2 mg/l. However, the linearity of the curve may depend on the type of instrumentation used and for this reason the linearity must be checked. If the calibration curve deviates from linearity the calibration standard given in step L7.10 is not appropriate. In such a case the calibration standard chosen for step L7.10 should be the highest concentration of the linear part of the calibration curve and the concentration range of the method should be adjusted accordingly. See also refs 21 and 40.

L9 Sources of Error

The principle sources of error in the method are similar to those encountered in the procedure for the detemination of dissolved chromium (Method K Section K11). If interference from other elements is suspected calibration should be carried out by the method of standard additions.

Analytical Quality Control

It is strongly recommended that a continuous check on analytical errors be made once any method has been established in routine use. Quality control charts provide a simple means of maintaining this check. Their principles, construction and use are described in Ref 62. For these methods, it is recommended that a control chart be maintained using a 'clean' offshore seawater collected in bulk, acidified to pH 2.5 or less (to stabilize during storage) and spiked with concentrations of the determinands of interest, near the upper limit of the range; the spiking solutions should originate from different stock standards to those used to make up the calibration standards.

Estimation of the Accuracy of Analytical Results using these Methods

1 Introduction

All the methods given in this booklet have only been thoroughly investigated in one or two laboratories. 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 findings to the Secretary of the Department of the Environment's Standing Committee of Analysts.

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.

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 determinand 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 of 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 low concentration
4	Standard solution high concentration
5	Typical sample
6	Same sample spiked with a known amount of determinand.

It is essential that these solutions be treated exactly as if they were samples and the appropriate specified procedure 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 be treated exactly as routine 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. The results of the

analyses of solutions 5 and 6 will provide a check of the effect of sample type on precision. Any deviation of the recovery of spiked metal from 100% may give an indication of the presence of interfering substances.

Note that the Blank water quality should be appropriate for the method being evaluated.

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.

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

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

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

$$s = \sqrt{\frac{(\bar{x}_1 - \bar{x})^2}{n-1}}$$

where x_1 = the result from the ith batch

$\bar{x}$ = the mean value of x_i.

3.4 Calculate the within-batch standard deviations, s_w, of the blank from:

$$S_w = \sqrt{\frac{\sum(\bar{x}_{1i} - \bar{x}_{2i})^2}{2n}}$$

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

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

3.5 Calculate the mean percentage recovery, R, of the spiked metal 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.

3.6 Summarize the results as in the following table:

Solution	No of results n	Mean metal Concentration	Standard Deviation	Mean Recovery %
2 Blank				—
3 Standard, low				—
4 Standard, high				—
5 Sample				—
6 Solution 5 + spike				

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

4 Evaluation of Interference Effects

If interference effects are suspected, analyse a series of standard samples with and without known amounts of interference plus also real samples, spiked real samples and spiked real samples with interferent added. If interference removal is contemplated, this should be evaluated in the same way.

There is a serious possibility of interference from dissolved organic matter in many, if not all, of these methods. Validation of digestion procedures is therefore important.

It should be borne in mind that the standard additions calibration recommended in many of the methods will not necessarily overcome inferferences by organics because there may not be sufficient time for equilibration of the spiked metal with any organic ligands not destroyed by digestion. These ligands may nonetheless affect the determination of the naturally present determinand. Information demonstrating that the recommended digestion procedure is indeed effective in overcoming interferences is therefore very important. If any laboratories developing these methods have data on the analysis of natural samples of known concentration, it is vital to include it. Results for analyses of reference samples, either obtained as Standard Reference Materials or prepared in house by spiking a natural sample (chosen to be representative as regards matrix but of low determinand concentration), or samples used in interlaboratory tests, would be valuable.

Some check on the effectiveness of the destruction of organics should be included as a quality control measure (eg I8.2.1 to I8.2.5). It is important that such AQC should be a routine feature of the methods since the efficiency of UV lamps and possibly of ozone generators cannot be relied upon over a long period of time. It is suggested that irradiation/ozonolysis of a solution of a test organic compound be included in each batch of analyses, with a check on UV absorbance. The above check must be validated by establishing that the measure of the effectiveness of digestion used on a routine basis is satisfactory for the removal of interfering substances.

References

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

(2) Grashoff K, *Methods of Seawater Analysis*, Verlag Chemie, 1976.

(3) Cooper L H N, *J Mar. Res*, **17**, 128–132, 1958.

(4) Williams P M, Robertson K J, Chenk and Weiss H V, *Mar. Chem*, **2**, 287–299, 1974.

(5) Brewer P G *et al*, *Mar. Chem*, **2**, 69–84, 1974.

(6) Riley J P in *Chemical Oceanography, 2nd Edn. Vol 3* Edit. Riley and Skirrow, Academic Press, 1975.

(7) Erickson P, *National Research Council of Canada Report NCCC 16472*, 1977.

(8) Segar D A and Berberian G A, *ACS Advances in Chemistry Series*, **147**, 9–16, 1975.

(9) Batley G E and Gardner D, *Water Research*, **11**, 745–756, 1977.

(10) Moody J R and Lindstrom R M, *Anal. Chem*, **49**, 14, 1977.

(11) Subramanian K S, Chakrabarti C L, Eneiras J E and Maineo I S, *Anal. Chem*, **50**, 3, March 1978.

(12) Laxen D P H and Harrison R M, *Anal. Chem*, **53**, 2, 1981.

(13) Agmenian H and Chau Y K, *Analyst*, **101**, 761–767, 1976.

(14) Sinex *et al*, *Anal. Chem*, **52**, 2342–2346, 1980.

(15) Tessier A *et al*, *Anal. Chem*, **51**, 844, 1979.

(16) *A Survey of Multielement and Related Methods of Analysis for Waters, Sediments and Other Materials of Interest to the Water Industry 1980*, HMSO, in this series.

(17) *Aluminium in Waters (Second Edition) 1987*. HMSO, in this series.

(18) *Cadmium, Chromium, Copper, Lead, Nickel and Zinc in Sewage Sludge by Nitric Acid/Atomic Absorption Spectrophotometry 1981*. HMSO, in this series.

(19) *Lead and Cadmium in Fresh Waters by Atomic Absorption Spectrophotometry. A General Introduction to EAAAS 1986*, HMSO, in this series.

(20) *Chromium in Raw and Potable Waters and Sewage Effluents 1980*, HMSO, in this series.

(21) *The Determination of Metals in Solids, Sediments, and Sewage Sludge, by Hydrochloric—Nitric Acid Digestion with a note on the Determination of Insoluble Metal Contents 1986*, HMSO in this series.

(22) *Metals in Waters by Electrothermal Atomization AAS 1988*, HMSO, in this series.

(23) *Cobalt in Potable Waters 1981*, HMSO, in this series.

(24) *Copper in Potable Waters by AAS 1980*. HMSO, in this series.

(25) *Iron in Potable Waters by Spectrophotometry 1977*. HMSO in this series.

(26) *Manganese in Raw and Potable Waters by Spectrophotometry 1977*. HMSO, in this series.

(27) *Nickel in Potable Waters 1981*. HMSO, in this series.

(28) *Zinc in Potable Waters by AAS 1980*. HMSO, in this series.

(29) *Mercury in Waters, Effluents and Sludge by Flameless AAS 1978.* HMSO, in this series.

(30) *Mercury in Waters (additional methods) 1985.* HMSO in this series.

(31) *Antimony in Effluents, Raw, Potable and Sea Waters by Spectrophotometry 1982.* HMSO, in this series.

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(34) *Measurement of Alpha and Beta Activities of Water Samples and Sludges; the Determination of Radon 22 and Radium 226; the Determination of Uranium (including General X-ray Fluorescent Spectrometric Analysis) 1985.* HMSO, in this series.

(35) Campbell J A, Cowling S J, Gunn A M, *WRC TR 227.* Water Research Centre, Medmenham 1985.

(36) Yates J. *Water Research Centre Technical Report 181.* Water Research Centre, Medmenham 1982.

(37) *Iron and Manganese in Waters 1983.* HMSO, in this series.

(38) Bryan, G W and Hummerstone, L G, *J Mar Biol Ass. UK*, **53**, 706, 1973.

(39) Martin A E, *Anal Chem*, **25**, 1260, 1953.

(40) Thompson M, and Howarth R J *Analyst*, **98**, 153, 1973.

(41) Cosovic B, and Vojvodic V. *Limnol, Oceanogr.*, **27**, 361–369, 1982.

(42) Gillain G, Duyckaerts G and Distech *Anal. Chim. Acta*, **106**, 23–37, 1979.

(43) Van den Berg C M G. *Anal. Chim. Acta*, **164**, 195–207, 1984.

(44) Van den Berg C M G and Huang Z Q. *Anal. Chem*, **56**, 2383–2386, 1984.

(45) Van den Berg C M G *Talanta*, **31**, 1069–1073, 1984.

(46) Pihlar B, Valenta P and Nurnberg H W. *Fresenius Z, Anal. Chem.*, **307**, 337–346, 1981.

(47) Adeloju S B, Bond A M and Briggs M H. *Anal. Chim. Acta*, **164**, 181–194, 1984.

(48) Van den Berg C M G and Nimmo M. *Anal. Chem.*, **56**, 924–8, 1987.

(49) Van den Berg C M G, Murphy K and Riley J P. *Anal. Chim. Acta*, **188**, 177–186, 1986.

(50) Apte S C, and Gunn A M, *Anal. Chim. Acta*, **193**, 147–156, 1987.

(51) Adeljou S B and Bond A M, *Anal. Chem.*, **57**, 1728–1733, 1985.

(52) Bruland K W, Franks R P, Knauer G A and Martin J H, *Anal. Chim. Acta*, **105**, 233–245, 1979.

(53) Sturgeon R E, Berman S S, Desaulaier A and Russel D S. *Talanta*, **27**, 85–94, 1980.

(54) Harper D and Riley J P. *WRC TR 215* Water Research Centre, Medmenham, 1985.

(55) Cranston R E, Murray J W. *Anal. Chim. Acta*, **99**, 175–282, 1978.

(56) Harper D. *PhD Thesis*, U of Liverpool.

(57) *General Principles of Sampling (2nd Edition); The Sampling of Rivers, Streams, Lakes, Reservoirs and Marine Waters, The Determination of Flow and Load 1988*, HMSO in this series.

(58) *Emission spectrophotometric Multielement Methods of Analysis for waters, Sediments etc 1980.* HMSO in this series.

(59) Chalmers R A. *Talanta*, **29**, 963–1055, 1980.

(60) Price W F. *Spectrochemical Analysis by Atomic Absorption*, Heyden, London 1979.

(61) Batley G E and Farrer Y G, *Anal. Chim. Acta*, **99**, 283–292, 1978.

(62) Cheeseman R V and Wilson A L—*WRC TR66* Water Research Centre, Medmenham 1978 (being revised).

(63) Nimmo, M. *Trace metal speciation in natural waters. PhD Thesis*, University of Liverpool (1987).

(64) Ward D. *Chemistry and Industry*, **(5)**, 7 March 1983, 211–2.

(65) Harper D J, Fileman C F, May P V, and Portmann J E, *Methods for the Analysis of Trace Metals in Marine and Other Samples*. Aquatic Environmental Analysis Methods. MAFF Fisheries Laboratory, Lowestoft (in press 1988).

(66) Cheek G T and Nelson R F. *Anal. Lett.* **A11.5**. 393–402, 1978.

(67) Golimowski J, Valenta S and Nurnberg H W. *Fres. Z. Anal. Chem.*, **322**, 315–322, 1985.

(68) Newton M P, and Vanden Berg C M G, *Anal. Chim. Acta*, **199**, 59–76. 1987.

(69) Hua C, Jagner D and Remnan L, *Anal. Chim. Acta*, **197**, 257–264. 1987.

(70) Hua C, Jagner D and Remnan L, *Anal. Chim. Acta*, **192**, 103–108. 1987.

(71) Van den Berg C M G, *J Electroanalytical Chem*, **215**, 111–121. 1986.

(72) Van den Berg C M G, and Nimmo M, in press.

(73) Capodaglio G, Van den Berg C M G, and Scarponi G, *J Electroanalytical Chem*, **235**. 275–286. 1987.

(74) Van den Berg C M G, *Anal. Chem*, **57**. 1532–1536. 1985.

(75) Van den Berg C M G and Khan S, in press.

(76) Wang J and Zadeii J M, *Anal. Chem Acta*, **185**. 229–238. 1986.

(77) Florence T M, Batley G E and Farras Y J, *J Electroanalytical Chem*, **56**. 301–309. 1974.

(78) Karpinski Z J, Polosac A, and Kublic Z, *Anal. Chem Acta*, **120**, 55–64. 1980.

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