

# Cadmium in Potable Waters

## by Atomic Absorption Spectrophotometry 1976

### Tentative Method

#### Methods for the Examination of Waters and Associated Materials

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## Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in a properly equipped laboratory. 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 others. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specification for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. One such publication is 'Code of Practice for Chemical Laboratories' issued by the Royal Institute of Chemistry, London. Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life, but that incorrect treatment can make

matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or 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.

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 the correct protective clothing or goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first aid, fire-fighting, and rescue equipment. If in doubt it is safer to assume that a hazard may exist and take reasonable precautions than to assume that no hazard exists until proved otherwise.

## About this series

This booklet is one of a series intended to provide recommended methods for the determination of water quality. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, has issued volumes of methods for the analysis of water and sewage culminating in '*Analysis of Raw, Potable and Waste Waters*'. These volumes, inevitably, took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being used when necessary. The ultimate aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users - the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has eight 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 Instrumentation and on-line analysis
- 3.0 Empirical and physical methods
- 4.0 Metals and metalloids
- 5.0 General non-metallic substances
- 6.0 Organic impurities
- 7.0 Biological methods
- 8.0 Sludge and other solids analysis

The actual methods etc are produced by small panels of experts in the appropriate field, under the overall supervision of the appropriate working group and the main committee. The names of those associated with this method are listed inside the back cover.

Publication of new or revised methods will be notified to the technical press, whilst a list of Methods in Print is given in the current HMSO Sectional Publication List No 5, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

TA DICK  
*Chairman*

LR PITTWELL  
*Technical Secretary*

4 November 1976

# Cadmium in Potable Waters by Atomic Absorption Spectrophotometry Tentative Method (1976 version)

## 1 Performance Characteristics of the Method

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

Note: Throughout this method cadmium is expressed as the element (Cd).

1.1	Substance determined	All forms of cadmium likely to occur in potable waters (see Sections 2 and 8).	
1.2	Type of sample	Potable waters.	
1.3	Basis of method	Extraction of pyrrolidine dithiocarbamate-cadmium into 4-methylpentan-2-one followed by atomic absorption spectrophotometry.	
1.4	Range of application (a)	Up to 10 µg/l (see Section 12).	
1.5	Calibration curve (a)	Linear to 10 µg/l (see Section 11).	
1.6	Standard deviation (a)*	Cadmium concentration (µg/l)	Standard deviation (µg/l)
		0.0	0.07 (b)
		10.0	0.30 (b)
		(each estimate has approximately 8 degrees of freedom).	
1.7	Limit of detection (a)*	0.3 µg/l (with 10 degrees of freedom).	
1.8	Sensitivity (a)	10 µg/l gives an absorbance of approximately 0.10.	
1.9	Bias	Not known.	
1.10	Interferences	Zinc (>5 mg/l) may interfere (see Section 3).	
1.11	Time required for analysis (a)	The total analytical and operator times are the same. Typical times for 1 and 10 samples are approximately 2.25 and 3.0 hours respectively excluding any pretreatment time (see also step 9.7).	

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

(b) Deionised water and tap water spiked with the stated cadmium concentration.

\* These data were obtained using this method without the pretreatment procedure.

## 2 Principle

2.1 The method described is based on experimental work carried out by the Water Research Centre (Medmenham Laboratory)<sup>(1)</sup>. Lead is extracted quantitatively together with cadmium and both elements may, if required, be determined in the same solvent extract (see lead method in this series).

2.2 Some samples may require pretreatment (see Section 8) by boiling with nitric acid to convert cadmium to forms capable of reacting with ammonium pyrrolidine dithiocarbamate (APDC). The cadmium chelate formed by reaction with APDC is extracted into 4-methylpentan-2-one (methyl isobutyl ketone - MIBK) and the amount of cadmium in the extract is determined by atomic absorption spectrophotometry by aspirating directly into the flame.

## 3 Interferences

Substances usually present in potable waters at their normal concentrations do not cause interference. However, low recoveries of cadmium have been reported<sup>(2)</sup> when zinc is present at a concentration greater than 5 mg/l. This effect can be overcome by dilution of the sample prior to carrying out the procedure in Section 9, so that the concentration of zinc is reduced below 5 mg/l. This results in some loss of sensitivity.

## 4 Hazards

The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away. One of the reagents, 4-methylpentan-2-one (MIBK) is flammable and has a harmful vapour (see Section 5.5). It is irritating to the eyes and mucous membranes and is narcotic in high concentrations. It must not be pipetted by mouth.

## 5 Reagents

All reagents and standard solutions should be kept in polyethylene bottles unless otherwise stated (see Section 6.3). Analytical reagent grade chemicals are suitable unless otherwise specified.

### 5.1 Water

The water used for blank determinations and for preparing reagents and standard solutions should have a cadmium content that is negligible compared with the smallest concentration to be determined in the samples (see Section 13.2). Deionized water or water distilled from an all glass apparatus is suitable.

### 5.2 50% V/V Hydrochloric acid

Dilute 500 ± 5 ml of hydrochloric acid (d<sub>20</sub> 1.18) with water to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

#### 5.2.1 3% V/V Hydrochloric acid

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

### 5.3 Nitric acid (d<sub>20</sub> 1.42)

#### 5.3.1 10% V/V Nitric acid

Dilute 100 ± 1 ml of nitric acid (d<sub>20</sub> 1.42) with water to 1 litre in a measuring cylinder. Store in a polyethylene bottle.

### 5.4 1% m/V Ammonium pyrrolidine dithiocarbamate (APDC)

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

### 5.5 4-Methylpentan-2-one (MIBK)

This reagent is hazardous (see Section 4). It is flammable and has a harmful vapour. A special grade of this solvent for atomic absorption spectrophotometry is preferable. Alternatively other grades may be purified by distillation in an all borosilicate glass apparatus. Adequate precautions must be taken during distillation including carrying it out over a distillation tray. MIBK should be stored in a glass bottle.



### 5.6 10% m/V Sodium hydroxide

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

### 5.7 0.1% m/V Bromophenol blue solution

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

### 5.8 Standard cadmium solutions

#### 5.8.1 Solution A 1 ml is equivalent to 100 $\mu$ g Cd

Weigh  $100.0 \pm 0.5$  mg of cadmium wire (greater than 99.9% purity) and dissolve with gentle heating in a mixture of  $7.0 \pm 0.5$  ml of nitric acid ( $d_{20}$  1.42) and approximately 20 ml of water. Quantitatively transfer the solution to a 1-litre calibrated flask, dilute with water to the mark and mix well. Store in a polyethylene bottle. This solution is stable for several months.

#### 5.8.2 Solution B 1 ml is equivalent to 0.2 $\mu$ g Cd

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

## 6 Apparatus

6.1 An atomic absorption spectrophotometer equipped for an air/acetylene flame and with a cadmium hollow cathode lamp. A chart recorder is the most desirable form of read-out. Scale expansion should be used to ensure that adequate recorder response is achieved with the highest calibration standard used.

### 6.2 Special apparatus

Glass tubes 20  $\times$  50 mm for the collection of the organic phases after the solvent extraction of the samples. These tubes should be fitted with snap-on polyethylene lids.

400-ml graduated borosilicate glass beakers.

250-ml glass separating funnels fitted with ground glass stoppers and taps.

### 6.3 Cleanliness

Cleanliness is essential for this determination. If possible, apparatus should be reserved solely for cadmium determinations: all residual cadmium from previous cadmium determinations must be removed. Clean all new glass and polyethylene ware by filling with or soaking in 10% V/V nitric acid for 2 days. Rinse thoroughly with water. Thereafter a thorough rinse in 10% V/V nitric acid followed by a thorough rinse with water after each determination should suffice.

## 7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section 6.3, add  $2.00 \pm 0.05$  ml of 50% V/V hydrochloric acid per litre of sample to be collected and then collect the sample. The acidification minimizes the adsorption of cadmium onto the walls of the bottle. Under certain circumstances (eg sampling by a householder) it may be necessary to modify the sampling procedure. When it is known that pretreatment will not be necessary (see Section 8) it is satisfactory to add to the empty bottle sufficient 50% V/V hydrochloric acid to bring the collected sample to pH  $2.5 \pm 0.3$ . It is then necessary to start the analytical procedure at step 9.5 by placing  $200 \pm 1$  ml of the sample in the separating funnel.

## 8 Sample Pretreatment

Samples containing suspended and/or colloidal material may require pretreatment to convert cadmium to an extractable form. A few organic cadmium compounds may not be converted by this procedure. Experience will indicate to analysts whether pretreatment is necessary for certain waters. The pretreatment procedure is given in steps 9.1 and 9.2.

## 9 Analytical Procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	<b>Analysis of samples</b>	
	<i>Pretreatment stage (note a)</i>	
9.1	Add $200 \pm 1$ ml of the sample (note b) to a 400-ml graduated borosilicate glass beaker. Add $1.0 \pm 0.1$ ml of nitric acid ( $d_{20}$ 1.42). Cover the beaker with a watch glass and simmer on a hot plate until the solution volume is reduced to $20 \pm 5$ ml (note c).	(a) If pretreatment is not required (see Section 8) add $200 \pm 1$ ml of sample to a 400-ml graduated borosilicate glass beaker and start at step 9.3, but omit step 9.4. This will result in a volume slightly greater than 200 ml, but it will not significantly affect the final result. (b) See Section 12 for the concentration range of the method. The zinc concentration in the sample must be less than 5 mg/l; if it is higher the sample must be diluted accordingly and an appropriate allowance made in the calculation of the result. (c) Great care must be taken during this step to minimize contamination (see Section 13).
9.2	Cautiously wash down the watch glass and sides of the beaker with water until the total volume in the beaker is $150 \pm 5$ ml. Replace the watch glass and allow the solution to cool to ambient temperature.	
	<i>Solvent extraction stage</i>	
9.3	Add 3 drops of 0.1% m/V bromophenol blue solution and, whilst swirling, slowly add 10% m/V sodium hydroxide until a blue colour persists. Whilst swirling, add 3% V/V hydrochloric acid dropwise until the blue colour is just discharged. Then add $2.0 \pm 0.1$ ml of 3% V/V hydrochloric acid (note d).	(d) Experience shows that the pH value at the end of step 9.3 should be $2.5 \pm 0.3$ . Very occasionally solutions may require readjustment to this value.
9.4	Transfer the solution to a measuring cylinder and dilute with water to $200 \pm 1$ ml (note e).	(e) The aqueous volume affects the final result. A constant 200 ml is therefore used.
9.5	Transfer the solution to a separating funnel. Add $4.00 \pm 0.05$ ml of APDC solution and shake to mix. Add $10.00 \pm 0.05$ ml of MIBK (notes f and g) and stopper the funnel.	(f) MIBK has a harmful vapour and must not be pipetted by mouth. (g) If other elements, eg lead, are to be determined on the same aliquot of the sample, up to 25 ml of MIBK may be used <i>throughout</i> . However, there will be considerable loss of sensitivity and possibly also of precision.
9.6	Shake the funnel vigorously for 2 min $\pm$ 15 s. Allow to stand for 5 min $\pm$ 30 s and then separate and discard the aqueous phase.	
9.7	Run the organic phase into a sample tube and fit the lid (note h). Complete the atomic absorption stage during the same working day.	(h) All samples, blanks and standards should be processed to this stage before proceeding to the atomic absorption stage.
	<b>Blank determination</b>	
9.8	A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples. To a 400-ml graduated borosilicate glass beaker add $0.40 \pm 0.05$ ml of 50% V/V hydrochloric acid and $200 \pm 1$ ml of water.	

Step	Experimental Procedure	Notes
9.9	If the pretreatment stage was used for the samples, carry out steps 9.1 to 9.7 inclusive. If not, carry out steps 9.3 and 9.5 to 9.7 inclusive.	
	<b>Calibration standards</b>	
9.10	Duplicate calibration standards must be run with each batch (eg up to 10 samples) of determinations (see Section 13.4). To a 500-ml calibrated flask add $1.00 \pm 0.05$ ml of 50% V/V hydrochloric acid. Pipette into the flask 25.0 ml of standard cadmium solution B, dilute with water to the mark and mix well. Place $200 \pm 1$ ml of this solution in a 400-ml graduated borosilicate glass beaker.	
9.11	If the pretreatment stage was used for the samples, carry out steps 9.1 to 9.7 inclusive. If not, carry out steps 9.3 and 9.5 to 9.7 inclusive.	
	<b>Atomic absorption stage</b>	
9.12	Set up the instrument according to the manufacturer's instructions for aspirating organic solvents into an air/acetylene flame. The wavelength required is 228.8 nm.	
9.13	Aspirate pure MIBK and adjust the zero. Aspirate one of the calibration standards (notes i and j) and adjust the instrument to give a suitable response, eg approximately 80% of full scale deflection.	(i) Keep the aspiration tube above the bottom of the sample tube to avoid aspiration of water which may have collected in the bottom of the sample tube. (j) Do not aspirate more than one third of the organic phase at this stage as it is required for 2 further aspirations.
9.14	Aspirate pure MIBK and readjust the zero if necessary. Re-aspirate both the calibration standards with an aspiration of pure MIBK after each and measure the maximum instrument responses $C_1$ and $C_2$ (eg peak height).	
9.15	Aspirate the blank (note i) and then pure MIBK and measure the maximum instrument response $B_1$ . Aspirate the samples (note i) with an aspiration of pure MIBK after each. Measure the maximum instrument response of the sample, S.	
9.16	To check for any instrument drift aspirate both the calibration standards and the blank with an aspiration of pure MIBK after each and measure the maximum instrument responses (eg peak height) $C_3$ , $C_4$ and $B_2$ respectively. If $C_1$ , $C_2$ , $C_3$ and $C_4$ and also $B_1$ and $B_2$ are in satisfactory agreement calculate the means $\bar{C}$ and $\bar{B}$ .	

Step	Experimental Procedure	Notes
	<b>Calculation of results (see Section 12)</b>	
9.17	Calculate the concentration, A, of cadmium in the sample from	
	$A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 10 \mu\text{g/l}$	
	where $\bar{C} = \frac{C_1 + C_2 + C_3 + C_4}{4}$	
	$\bar{B} = \frac{B_1 + B_2}{2}$	
	This calculation assumes a linear calibration curve. Linearity must be checked (see Section 11).	
<b>10</b>	<b>Measurement of Maximum Instrument Responses</b>	The maximum instrument responses for samples, standards and blanks are measured with respect to the response of pure MIBK aspirated on either side. The following example is for the measurement of peak height when a chart recorder is in use.  Draw a line on the chart through the traces for the pure MIBK bracketing the peak height to be measured. Draw a line through the trace corresponding to the equilibrium response of that peak height, and measure the perpendicular separation of the two constructed lines using a ruler. When the recorder traces show short-term variations, it is suggested that the lines be drawn through the visually estimated mid-points of the equilibrium portions of the traces.
<b>11</b>	<b>Checking the Linearity of the Calibration Curve</b>	The procedure given in this section must be carried out on at least two independent occasions before application of this method to any samples and regularly thereafter.  To each of a series of 500-ml calibrated flasks add $1.00 \pm 0.05$ ml of 50% V/V hydrochloric acid. Pipette respectively to these flasks 0.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml of standard cadmium solution B and dilute with water to the mark. These flasks contain respectively 0, 2, 4, 6, 8 and 10 $\mu\text{g/l}$ cadmium. Place $200 \pm 1$ ml of these solutions in a series of 400-ml graduated borosilicate glass beakers and carry out the procedure given in steps 9.3, 9.5 to 9.7 inclusive and steps 9.12 to 9.16 inclusive. Plot the maximum instrument response (eg peak height) against $\mu\text{g/l}$ cadmium.  The calibration curve is normally linear to 10 $\mu\text{g/l}$ cadmium; however, the linearity of the curve may depend on the type of instrumentation used and therefore linearity must be checked. If the calibration curve departs from linearity the calibration standard in step 9.10 is not appropriate, nor is the range given in Section 1.4. In such a case the calibration standard chosen for step 9.10 should be the highest concentration on the linear portion of the calibration curve and the concentration range of the method should be adjusted accordingly.
<b>12</b>	<b>Change of Concentration Range of the Method</b>	If the cadmium concentration in the sample is likely to exceed 10 $\mu\text{g/l}$ an appropriately smaller aliquot of the sample must be taken for analysis. To this volume of sample, V ml, add sufficient 50% V/V hydrochloric acid so that there is the same total volume of 50% V/V hydrochloric acid present as there would be in 200 ml of sample. Dilute with water to 200 ml and proceed as in step 9.1 onwards. It is necessary to alter the calculation of the result, step 9.17, as follows: $A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 10 \times \frac{200}{V} \mu\text{g/l cadmium}$

### 13 Sources of Error

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

#### 13.1 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of cadmium or its compounds are handled. The technique and working conditions should be critically examined and any sources of contamination eliminated or minimized. In particular, it is desirable to reserve the glass apparatus used for the cadmium determinations solely for this purpose and to carry out a preliminary series of blank determinations to ensure low blank values before analysing any samples.

#### 13.2 Cadmium content of the water used for blank determinations

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

- (a) To each of two 500-ml borosilicate glass beakers add  $200 \pm 5$  ml of water and  $0.40 \pm 0.05$  ml of 50% V/V hydrochloric acid.
- (b) To each of two 500-ml borosilicate glass beakers add  $400 \pm 10$  ml of water and  $0.40 \pm 0.05$  ml of 50% V/V hydrochloric acid.
- (c) Cover all beakers with clean watch glasses and heat those from (b) on a hot plate until the volumes in them have been reduced to approximately 200 ml. Add a further  $200 \pm 5$  ml of water to each beaker from (b) and continue heating until the volumes are reduced to  $200 \pm 5$  ml. Cool the solution to room temperature.
- (d) Analyse the contents of all four beakers as described in Section 9 and let the measured maximum instrument responses be  $W_1^1$  and  $W_2^1$  for the two unheated beakers and  $W_1^{11}$  and  $W_2^{11}$  for the two heated beakers.
- (e) The cadmium content of the blank water is equivalent to a maximum instrument response of

$$W = \frac{(W_1^{11} + W_2^{11}) - (W_1^1 + W_2^1)}{4}$$

- (f) The concentration of cadmium,  $A_w$ , in the blank water is the given by

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

(see step 9.17).

#### 13.3 Interfering substances

See Section 3. The effect of possible interfering substances may be determined by analysing samples spiked with cadmium and various concentrations of the potential interfering substance.

#### 13.4 Calibration standards

The calibration curve for this method has been found to be linear though its slope may vary from one set of determinations to another. Such variations are caused by changes in the sensitivity of the atomic absorption spectrophotometer. Therefore a calibration standard must be run for each batch of analyses and step 9.10 onwards gives the necessary procedure. This procedure assumes a linear calibration curve and the linearity must be checked (see Section 11).

### 14 Checking the Accuracy of Analytical Results

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

Once the methods have been put into normal routine operation many factors may subsequently adversely affect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of tests are possible and they should be used as appropriate. As a minimum, however, it is suggested that a standard solution of cadmium of suitable concentration should be analysed at the same time and in exactly the same way as normal samples (see Section 5.8.2 and step 9.10). The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate accuracy, and will also allow the standard deviation of routine analytical results to be estimated.

### 15 References

- (1) Water Research Association, Medmenham, *Technical Inquiry Report*, TIR No 254, August 1972.
- (2) Department of the Environment, File WS/646/7, Paper SCA/MG/75/66, September 1975.



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

### 1 Introduction

Quantitative investigation of the accuracy achievable when the cadmium method is used appears to be limited to work at the Water Research Centre (Medmenham Laboratory). Before firmly recommending the method for general use, it is desirable to know the accuracy achievable in other laboratories. It would, therefore, be of great value if any laboratory using or considering the use of this method could estimate the accuracy of its own analytical results and report the findings to the Technical Secretary of the Metals and Metalloids Working Group 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 cadmium in the sample analysed and on the type of sample, eg worse precision may be obtained with samples than with standard solutions. For these reasons the basic design recommended is the analysis of one portion 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 1.0 $\mu\text{g/l}$ Cd
4	Standard solution 10.0 $\mu\text{g/l}$ Cd
5	Typical sample
6	Same sample spiked with 10.0 $\mu\text{g/l}$ Cd

It is essential that these solutions be treated exactly as if they were samples and the procedure specified in Section 9 of the method be rigidly followed. These solutions should be analysed in random order in each batch of analyses. Solutions 1 to 4 should be prepared each day exactly as described in the method and should contain the same amount of hydrochloric acid as is present in the samples. The same batch of water should be used on each day to prepare all four solutions. For solutions 5 and 6 a total of 5 litres of typical sample are required. Prepare solution 6 each day when required by spiking solution 5 as follows: add with a bulb pipette 1.00 ml of an intermediate standard cadmium solution to 100 ml of solution 5. (The intermediate standard cadmium solution is prepared by diluting  $10.0 \pm 0.01$  ml of standard cadmium solution *A* with water to 100 ml in a calibrated flask.) When analysing solution 6 it will be necessary to take into account Section 12 and to take an appropriately smaller aliquot. The total period of the tests may be any convenient time so long as the cadmium concentration in solution 5 does not change appreciably (up to 2 weeks). The results of the analyses of solutions 5 and 6 will provide a check on the effect of sample type on precision. Any deviation of the recovery of spiked cadmium from 100% may give an indication of the presence of interfering substances.

### 3 Evaluation of Results

The raw experimental results should 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:

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

where  $x_i$  = the result from the  $i$ th batch

$\bar{x}$  = the mean value of  $x_i$ .

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

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

where  $x_{1i}$  = the 1st blank result (solution 1) from the  $i$ th batch

$x_{2i}$  = the 2nd blank result (solution 2) from the  $i$ th batch.

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

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

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

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

3.6 Summarize the results as in the following table:

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

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

\* Results to be sent to the following:

The Technical Secretary  
The Metals and Metalloids Working Group  
The Standing Committee of Analysts  
The Department of the Environment  
2 Marsham Street  
London SW1P 3EB  
England

### Address for Correspondence

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

The Technical Secretary  
The Standing Committee of Analysts  
The Department of the Environment  
2 Marsham Street  
LONDON SW1P 3EB  
England



Standing Committee of Analysts

Members of the Committee Responsible for this Method:

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Mr J Borland	after June 1975*
Dr JM Carter	after June 1975*
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