

Cobalt in Potable Waters 1981

Methods for the Examination of Waters and Associated Materials

Cobalt in Potable Waters Tentative Methods (1981 Version)

Methods for the Examination of Waters and Associated Materials

Two methods for the determination of cobalt in potable waters are described in order to cater for the availability of equipment in different laboratories. The first, Method A, is based on the extraction of pyrrolidine dithiocarbamate-cobalt into 4-methylpentan-2-one followed by atomic absorption spectrophotometry. The second, Method B, is based on concentration by evaporation followed by atomic absorption spectrophotometry.

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Warning to Users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local safety regulations must be observed. Laboratory procedures should be carried out only in properly equipped laboratories. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specification. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

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

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times

when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the 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 correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. If in doubt; it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

About this series

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

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods of 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 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 Instrumentation and on-line analysis
- 3.0 Empirical and physical methods*
- 4.0 Metals and metalloids
- 5.0 General nonmetallic substances
- 6.0 Organic impurities
- 7.0 Biological methods
- 8.0 Sludge and other solids analysis*
- 9.0 Radiochemical methods

The actual methods etc 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, and the current status of publication and revision will be given in the biennial reports of the Standing Committee of Analysts.

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 for booklets in this series are given in the Reports of The Standing Committee of Analysts, published by the Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9BT. 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 the booklet.

T A DICK
Chairman

L R PITTWELL
Secretary

25 September 1981

* These two working groups are in process of being wound up. Their tasks are being redistributed among the other working groups.

Cobalt in Potable Waters by Atomic Absorption Spectrophotometry Tentative Method (1980 Version)

Note: Throughout this method cobalt is expressed as the element (Co)

A1 Performance Characteristics of the Method

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

A1.1	Substance determined	All forms of cobalt likely to occur in potable waters (see Sections A2 and A8).		
A1.2	Type of sample	Potable waters.		
A1.3	Basis of the method	Extraction of pyrrolidine dithiocarbamate - cobalt into 4-methylpentan -2-one followed by atomic absorption spectrophotometry.		
A1.4	Range of application (a) (b)*	Up to 100 µg/l (See Section A11).		
A1.5	Calibration curve (a) (b)*	Linear to 100 µg/l (see Section A10).		
A1.6	Standard deviation* *	Cobalt concentration (µg/l)	Standard deviation (µg/l)	Degrees of freedom
	total	0.0 (a)	1.25	23
		2.5	0.58	44
		5.0	0.72	10
		25.0	1.24	34
		40.0	1.89	44
		50.0	1.84	23
		80.0	2.24	10
		0.0 (b)	0.19	11
		50.0	0.62	11
A1.7	Limit of detection (a) (b)	0.9 to 5.8 µg/l with 11 to 23 degrees of freedom.		
A1.8	Sensitivity (b)	50 µg/l gives an absorbance of approximately 0.22		
A1.9	Bias	None known.		
A1.10	Interferences	See Section A3.		
A1.11	Time required for analysis (a) (b)	The total analytical and operator times are the same. A typical time for a batch of 10 samples is 3.0 hours excluding any pre-treatment time.		

(a) These data were obtained at the Laboratory of the Government Chemist⁽¹⁾ using a double beam atomic absorption spectrophotometer and doubly distilled water spiked with the stated cobalt concentration.

(b) These data were obtained at Yorkshire Water Authority, Head Office Laboratory⁽²⁾ using a double beam atomic absorption spectrophotometer and deionized water spiked with the stated cobalt concentration.

* For some instruments the calibration curve is known to be linear to cobalt concentrations of less than 100 µg/l thus affecting the range of application. Analysts should check the linearity of the curve for their particular instrument (see Sections A10 and A11).

** These data were obtained using this method but without the pre-treatment procedure.

A2 Principle

A2.1 The method described is based on the reaction of cobalt with ammonium pyrrolidine dithiocarbamate (APDC) to form a cobalt chelate which is extracted into 4-methylpentan-2-one (methyl isobutyl ketone – MIBK). The amount of cobalt in the extract is determined by atomic absorption spectrophotometry by aspirating directly into the flame.

A2.2 Some samples may require pre-treatment (see Section A8) by boiling with nitric acid to convert cobalt to forms capable of reacting with APDC.

A2.3 Other elements, for example lead⁽³⁾, cadmium⁽⁴⁾ and nickel⁽⁵⁾ are extracted quantitatively together with cobalt and all these elements may, if required, be determined in the same solvent extract (see step A9.5, note g).

A3 Interferences

A3.1 The effect of other substances on the determination of cobalt by this method is shown in Table A1.

Table A1

Other substance	Other substance added as	Concentration of other substance (mg/l)	Effect in µg/l Co of other substance at a cobalt concentration of (d)		
			0 µg/l	50 µg/l	100 µg/l
			(a)	(a)	
Copper (as Cu ²⁺)	perchlorate	1	0.2	- 0.8	
”	”	2	0.1	+ 0.3	
”	”	5	4.2	+ 6.1	
Iron (as Fe ²⁺)	perchlorate	2		+ 2.5	
”	”	5	0.1	+ 1.5	
Manganese (as Mn ²⁺)	perchlorate	2		+ 4.0	
”	”	5	0.1	- 4.7	
”	nitrate	1		- 0.4	
Zinc (as Zn ²⁺)	nitrate	5	0.1	+ 4.7	
Nickel (as Ni ²⁺)	nitrate	5	4.4	- 0.8	
Sulphate (as SO ₄ ²⁻)	acid	1000	0.2	- 0.1	
				(b)	
Manganese (as Mn ²⁺)	nitrate	3		- 0.6	
”	”	4		- 2.1	
”	”	5		-44.5	
Zinc (as Zn ²⁺)	nitrate	1		0.0	
					(c)
Magnesium (as Mg ²⁺)	chloride	100			+ 3.4
Calcium (as Ca ²⁺)	chloride	200			+ 3.1
Sodium (as Na ⁺)	chloride	100			+ 0.6
Potassium (as K ⁺)	chloride	100			+ 1.2
Diethyl sulpho-succinate		1			- 0.1
”		2			- 8.6
”		5			- 5.8
Linear alcohol ethoxylate		1			- 1.4
”		5			+ 0.4
Laboratory glassware cleaning agent		1			- 0.4
”		5			+ 2.5
Orthophosphate (as PO ₄ ³⁻)	sodium	5			+ 1.0
”	”	20			+ 2.1
Metasilicate (as SiO ₃ ²⁻)	sodium	5			+ 0.5
”	”	20			+ 2.7

(a) These data were obtained at the Laboratory of the Government Chemist⁽¹⁾.

(b) These data were obtained at Yorkshire Water Authority, Head Office Laboratory⁽²⁾.

(c) These data were obtained at the Marine Biological Association Laboratory, Plymouth⁽⁶⁾.

(d) If the other substances did not interfere the effect would be expected (95% confidence) to lie within the range 0.00 ± 0.52 at 0 µg/l 0.00 ± 0.39 at 50 µg/l and 0.00 ± 5.00 at 100 µg/l cobalt.

A4 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 A5.5). It is irritating to the eyes and mucous membranes and is narcotic in high concentrations. It must not be pipetted by mouth.

A5 Reagents

All reagents and standard solutions should be kept in polyethylene bottles unless otherwise stated (see Section A6.3). Analytical reagent grade chemicals are suitable unless otherwise specified.

A5.1 Water

The water used for blank determinations and for preparing reagents and standard solutions should have a cobalt content that is negligible compared with the smallest concentrations to be determined in the samples (see Section A12.2). Deionized water or water distilled from an all glass apparatus is suitable.

A5.2 50% V/V Hydrochloric acid

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

A5.2.1 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.

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

A5.3.1 10% V/V Nitric acid

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

A5.4 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.

A5.5 4-Methylpentan-2-one (MIBK)

This reagent is hazardous (see Section A4). 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.

A5.6 10% m/V Sodium hydroxide

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

A5.7 0.1% m/V Bromophenol blue solution

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

A5.8 Standard cobalt solutions

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

Weigh accurately 1.000 ± 0.001 g of pure cobalt (rod, foil or wire) and dissolve by warming with 5 ± 1 ml of nitric acid (d_{20} 1.42) and 15 ± 1 ml of water. When dissolved, add 10 ± 1 ml of hydrochloric acid (d_{20} 1.18) and 100 ± 2 ml of water, cool and dilute with water to 1 litre in a calibrated flask. Store in a polyethylene bottle. This solution is stable for at least six months.

A5.8.2 *Solution B*. 1 ml contains 2 µg Co.

Pipette 2.00 ± 0.01 ml of *solution A* into a 1-litre calibrated flask and dilute with water to the mark. This solution should be freshly prepared before use.

A6 Apparatus

A6.1 An atomic absorption spectrophotometer equipped for an air-acetylene flame and a cobalt hollow cathode lamp.

A6.2 Special Apparatus

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

A6.3 Cleanliness

Cleanliness is essential for this determination. If possible, apparatus should be reserved solely for cobalt determinations: all residual cobalt from previous cobalt 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.

A7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section A6.3, add 2.00 ± 0.05 ml of 50% V/V hydrochloric acid per litre of sample to be collected and then collect the sample. The acidification minimizes the adsorption of cobalt, on to the walls of the bottle. Under certain circumstances (eg sampling by a house-holder) it may be necessary to modify the sampling procedure. When it is known that pretreatment will not be necessary (see Section A8) it is satisfactory to add to the empty bottle sufficient 50% V/V hydrochloric acid to bring the collected sample to pH 2.5 ± 0.3 . It is then necessary to start the analytical procedure at step A9.5 by placing 200 ± 1 ml of the sample in the separating funnel.

A8 Sample Pretreatment

Samples containing suspended and/or colloidal material may require pretreatment to convert cobalt to an extractable form. A few organic cobalt compounds may not be converted by this pretreatment procedure. Experience will indicate to analysts whether pretreatment is necessary for certain waters. The pretreatment procedure is given in steps A9.1 and A9.2.

A9 Analytical Procedure

READ SECTION A4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Analysis of samples	
	<i>Pretreatment stage (note a)</i>	
A9.1	Add 200 ± 1 ml of the sample (note b) to a 400-ml graduated borosilicate glass beaker. Add 1.0 ± 0.1 ml of nitric acid (d_{20} 1.42). Cover the beaker with a watch glass and simmer on a hot plate until the solution volume is reduced to 20 ± 5 ml (note c).	(a) If pretreatment is not required (see Section A8) add 200 ± 1 ml of sample to a 400-ml graduated borosilicate glass beaker and start at step A9.3, but omit step A9.4. This will result in a volume slightly greater than 200 ml, but it will not significantly affect the final result. (b) See Section A11 for the concentration range of the method. (c) Great care must be taken during this step to minimize contamination (see Section A12).

Step	Experimental Procedure	Notes
A9.2	Cautiously wash down the watch glass and the sides of the beaker with water until the total volume in the beaker is 150 ± 5 ml. Replace the watch glass and allow the solution to cool to ambient temperature.	
	<i>Solvent extraction stage</i>	
A9.3	Add 3 drops of 0.1% m/V bromophenol blue solution and, whilst swirling slowly, add 10% m/V sodium hydroxide until a blue colour persists. Whilst swirling, add 3% V/V hydrochloric acid dropwise until the blue colour is just discharged. Then add 2.0 ± 0.1 ml of 3% V/V hydrochloric acid (note d).	(d) Experience shows that the pH value at the end of step A9.3 should be 2.5 ± 0.3 . Very occasionally solutions may require readjustment to this value.
A9.4	Transfer the solution to a measuring cylinder and dilute with water to 200 ± 1 ml (note e).	(e) The aqueous volume affects the final result. A constant 200 ml is therefore used.
A9.5	Transfer the solution to a separating funnel. Add 4.00 ± 0.05 ml of APDC solution and shake to mix. Add 10.00 ± 0.05 ml of MIBK (notes f and g) and stopper the funnel.	(f) MIBK has a harmful vapour and must not be pipetted by mouth. (g) If other elements, eg cadmium, lead, nickel, are to be determined on the same aliquot of the sample, up to 25 ml of MIBK may be used throughout. However, there will be considerable loss of sensitivity and possibly also of precision.
A9.6	Shake the funnel vigorously for $2 \text{ min} \pm 15 \text{ s}$. Allow to stand for $5 \text{ min} \pm 30 \text{ s}$ and then separate and discard the aqueous phase	
A9.7	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.
	<i>Blank determination</i>	
A9.8	A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for the samples. To a 400-ml graduated borosilicate glass beaker add 0.40 ± 0.05 ml of 50% V/V hydrochloric acid and 200 ± 1 ml of water.	
A9.9	If the pretreatment stage was used for the samples, carry out steps A9.1 to A9.7 inclusive. If not, carry out steps A9.3 and A9.5 to A9.7 inclusive.	
	<i>Calibration standards</i>	
A9.10	Duplicate calibration standards must be run with each batch (eg up to 10 samples) of determinations (see Section A12.4). To a 500-ml calibrated flask add 1.00 ± 0.05 ml of 50% V/V hydrochloric acid. Pipette into the flask 25.0 ml of standard cobalt solution B dilute with water to the mark and mix well. Place 200 ± 1 ml of this solution in a 400-ml graduated borosilicate glass beaker.	
A9.11	If the pretreatment stage was used for the samples, carry out steps A9.1 to A9.7 inclusive. If not, carry out steps A9.3 and A9.5 to A9.7 inclusive.	

Step	Experimental Procedure	Notes
	Atomic absorption stage	
A9.12	Set up the instrument according to the manufacturer's instructions for aspirating organic solvents into an air/acetylene flame. The wavelength required is 240.7 nm.	
A9.13	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.
A9.14	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).	
A9.15	Aspirate the blank (note j) 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 .	
A9.16	To check for any instrument drift aspirate both calibration standards and the blank with an aspiration of pure MIBK after each and measure the maximum instrument responses (eg peak height). C_3 , C_4 and B_2 respectively. If C_1 , C_2 , C_3 and C_4 and also B_1 and B_2 are in satisfactory agreement calculate the means \bar{C} and \bar{B} .	
	Calculation of results (see Section A11)	
A9.17	Calculate the concentration, A , of cobalt in the sample from	
	$A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 100 \mu\text{g/l}$	
	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 A10.)	

A10 Checking the Linearity of the Calibration Curve

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

To each of a series of 500-ml calibrated flasks add 1.00 ± 0.05 ml of 50% V/V hydrochloric acid. Pipette respectively to these flasks 0.0, 5.0, 10.0, 15.0, 20.0 and 25.0 ml of standard cobalt solution B and dilute with water to the mark. These flasks contain respectively 0, 20, 40, 60, 80 and 100 $\mu\text{g/l}$ cobalt. Place 200 ± 1 ml of these solutions in a series of 400-ml graduated borosilicate glass beakers and carry out the procedure given in steps A9.3, A9.5 to A9.7 inclusive and steps A9.12 to A9.16 inclusive. Plot the maximum instrument response (eg peak height) against $\mu\text{g/l}$ cobalt.

The calibration curve is normally linear to 100 $\mu\text{g/l}$ cobalt, 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 A9.10 is not appropriate, nor is the range given in Section A1.4. In such a case the calibration standard chosen for step A9.10 should be the highest concentration on the linear portion of the calibration curve and the concentration range of the method should be adjusted accordingly.

A11 Change of Concentration Range of the Method

If the cobalt concentration in the sample is likely to exceed 100 $\mu\text{g/l}$ 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 A9.1 onwards. It is necessary to alter the calculation of the result, step A9.17, as follows:

$$A = \frac{S - \bar{B}}{C - \bar{B}} \times 100 \times \frac{200}{V} \mu\text{g/l cobalt}$$

A12 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 summarise the main sources of error.

A12.1 Contamination

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

A12.2 Cobalt content of the water used for blank determinations

If the water used for the blank determinations contains cobalt the results will be falsely low. The importance of this error depends on the cobalt concentration of the blank water and the concentrations of interest in the samples. Ideally the cobalt content of the water used for each blank determination should be measured and an appropriate correction made. An upper limit for the cobalt 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 nickel content of the water:

- To each of two 500-ml borosilicate glass beakers add 200 ± 5 ml of water and 0.40 ± 0.05 ml of 50% V/V hydrochloric acid.
- To each of two 500-ml borosilicate glass beakers add 400 ± 10 ml of water and 0.40 ± 0.05 ml of 50% V/V hydrochloric acid.
- Cover all beakers with clean watch glasses and heat those from (b) on a hot plate until the volumes in them have been reduced to approximately 200 ml. Add a further 200 ± 5 ml of water to each beaker from (b) and continue heating until the volumes are reduced to 200 ± 5 ml. Cool the solution to room temperature.

(d) Analyse the contents of all four beakers as described in Section A9 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 cobalt 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 cobalt, A_w , in the blank water is then given by

$$A_w = \frac{W}{\bar{C} - \bar{B}} \times 100 \mu\text{g/l cobalt}$$

(See step A9.17).

A12.3 Interfering substances

See Section A3. The effect of possible interfering substances may be determined by analysing samples spiked with cobalt and various concentrations of the potential interfering substance.

A12.4 Calibration standards

The calibration curve for this method has been found to be linear though its slope may vary from one set of determinations to another. Such variations are caused by changes in the sensitivity of the atomic absorption spectrophotometer. Therefore a calibration standard must be run for each batch of analyses and steps A9.10 onwards give the necessary procedure. This procedure assumes a linear calibration curve and the linearity must be checked (see Section A10).

A13 Checking the Accuracy of Analytical Results

(For further information see General Principles of Sampling and Accuracy of Results 1980, also published 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 cobalt of suitable concentration be analysed at the same time and in exactly the same way as normal samples (see Section A5.8.2 and step A9.10). 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.

A14 References

- (1) Department of the Environment, File WS/646/50, Papers SCA/42/5/2A to 2C.
- (2) Department of the Environment, File WS/646/50, Papers SCA/42/5/1A to 1D.
- (3) *Lead in Potable Waters by Atomic Absorption Spectrophotometry 1976*. Methods for the Examination of Water and Associated Materials, HMSO 1977.
- (4) *Cadmium in Potable Waters by Atomic Absorption Spectrophotometry 1976*. Methods for the Examination of Waters and Associated Materials, HMSO 1977.
- (5) *Nickel in Potable Waters by Atomic Absorption Spectrophotometry 1981*. Methods for the Examination of Waters and Associated Materials, HMSO, in press.
- (6) Department of the Environment, File WS/646/50, Papers SCA/42/5/3A and B.

B

Cobalt in Potable Waters by Atomic Absorption Spectrophotometry Tentative Method (1981 Version)

Note: Throughout this method cobalt is expressed as the element Co.

B1 Performance Characteristics of the Method.

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

B1.1	Substance determined	All forms of cobalt likely to occur in potable waters (see Sections B2 and B8)		
B1.2	Type of sample	Potable waters		
B1.3	Basis of the method	Concentration of the sample by evaporation followed by atomic absorption spectrophotometry.		
B1.4	Range of application (a)	Up to 100 µg/l (see Section B12)		
B1.5	Calibration curve (a)	Linear to 100 µg/l (see Section B11)		
B1.6	Standard deviation	Cobalt concentration (µg/l)	Standard deviation (µg/l)	Degrees of freedom
	B1.6.1 within batch	0.0 (a) (c)	0.66	9
		0.0 (a) (d)	0.30	9
		10.0 (a) (c)	0.53	9
		50.0 (a) (c)	0.91	9
		50.0 (a) (d)	1.36	9
		100.0 (a) (c)	1.67	9
		0.0 (b) (c)	0.31	9
		20.0 (b) (c)	0.49	5
		100.0 (b) (c)	1.20	5
	B1.6.2 total	0.0 (a) (c)	0.43	9
		0.0 (a) (d)	0.31	9
		10.0 (a) (c)	0.77	9
		50.0 (a) (d)	1.09	9
		100.0 (a) (c)	1.99	9
		0.0 (b) (c)	0.44	9
		20.0 (b) (c)	0.48	9
		100.0 (b) (c)	0.88	9
B1.7	Limit of detection (a)	1.1 (b) to 2.4 µg/l (a) each with 9 degrees of freedom.		
B1.8	Sensitivity (a)	100 µg/l gives an absorbance of about 0.1		
B1.9	Bias	Not known		
B1.10	Interferences	None of the metals commonly present in potable waters cause significant interference at moderate concentrations (see Section B3).		
B1.11	Time required for analysis (a)	The typical time for a batch of 10 to 15 samples is approximately 4 hours of which the evaporation stage occupies approximately 3 hours.		

- (a) These data were obtained at the Southern Division Water Pollution Control Laboratory, Yorkshire Water Authority⁽¹⁾
- (b) These data were obtained at the Marine Biological Association, Plymouth⁽²⁾
- (c) Deionized water spiked with the stated cobalt concentration.
- (d) Tap water spiked with the stated cobalt concentration.

B2 Principle

Cobalt is determined by atomic absorption spectrophotometry after concentration of the sample 10 times by evaporation in the presence of nitric acid. The pre-treatment by evaporation with nitric should ensure that any cobalt present in suspended or colloidal forms is converted into a soluble form. It is possible to determine other metals using this technique such as copper⁽³⁾, zinc⁽⁴⁾ and nickel⁽⁵⁾.

B3 Interferences

Most substances normally present in potable waters do not interfere. The effect of other substances on the method described has been determined by 2 laboratories^{(1) (2)} and is shown in table B1.

B4 Hazards

The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away.

B5 Reagents

All reagents may be kept in glass or polyethylene bottles (see Section B6.2). Analytical reagent grade chemicals are suitable unless otherwise stated.

B5.1 Water

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

B5.2 50% V/V Hydrochloric acid

Dilute 500 ± 5 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a stoppered measuring cylinder and mix well.

B5.3 Nitric Acid (d_{20} 1.42).

B5.3.1 5M Nitric Acid approximately

Dilute 320 ± 5 ml of nitric acid (d_{20} 1.42) with water to 1 litre in a stoppered measuring cylinder and mix well.

B5.3.2 10% V/V Nitric Acid

Dilute 100 ± 1 ml of nitric acid (d_{20} 1.42) with water to 1 litre in a stoppered measuring cylinder and mix well.

B5.4 Standard cobalt solutions

B5.4.1 Solution A 1 ml contains 1 mg Co

Weigh 1.000 ± 0.005 g of cobalt foil or powder (greater than 99.9% purity), and dissolve it in a mixture of 30 ± 1 ml of nitric acid (d_{20} 1.42), 30 ± 1 ml of hydrochloric acid (d_{20} 1.18) and approximately 50 ml of water, carrying out the operation in a fume cupboard. Quantitatively transfer the solution to a 1-litre calibrated flask, dilute with water to the mark and mix well. The solution is stable for at least several months. Alternatively use a commercially available standard cobalt solution.

B5.4.2 Solution B 1 ml contains 20 µg Co

Dilute 20.0 ml of *solution A* with water to 1 litre in a calibrated flask and mix well. This solution should be freshly prepared before use.

Table B1

Other substance		Concentration of other substance ($\mu\text{g/l}$)	Other substance added as	Effect in $\mu\text{g/l}$ Co of other substance at a cobalt concentration of (c)		
				0.0 $\mu\text{g/l}$	10.0 $\mu\text{g/l}$	50.0 $\mu\text{g/l}$
Calcium	(as Ca^{2+})	200	chloride	+4.5	+2.2	-2.6*
Magnesium	(as Mg^{2+})	20	chloride	-1.0	-0.3	-2.1
Sodium	(as Na^+)	100	chloride	+0.2	+0.8	+0.3
Calcium	(as Ca^{2+})	100	chloride)	+1.9	+0.9	-1.3
Magnesium	(as Mg^{2+})	25	chloride)			
Sodium	(as Na^+)	50	chloride)			
Potassium	(as K^+)	10	chloride)			
Copper	(as Cu^{2+})	5	chloride)	0.0	+0.6	-0.2
Zinc	(as Zn^{2+})	5	chloride)			
Manganese	(as Mn^{2+})	5	chloride)			
Iron	(as Fe^{3+})	5	chloride	-0.1	+1.2	+0.3
Sulphate	(as SO_4^{2-})	200	hydrogen	+0.3	-0.2	+0.4
Phosphate	(as PO_4^{3-})	20	ammonium dihydrogen	-0.4	+1.2	+1.4
Silicon	(as SiO_2)	10	sodium silico-fluoride	0.0	+1.0	-0.3
Non ionic detergent		10		+0.5	+1.1	+1.8
				0.0 $\mu\text{g/l}$	20.0 $\mu\text{g/l}$	100.0 $\mu\text{g/l}$
Aluminium	(as Al^{3+})	1	nitrate)			* *
Copper	(as Cu^{2+})	5	nitrate)			
Iron	(as Fe^{3+})	2	nitrate)	-0.4	-0.5	+3.4
Manganese	(as Mn^{2+})	2	nitrate)			
Zinc	(as Zn^{2+})	5	nitrate)			
Calcium	(as Ca^{2+})	300	chloride)	-0.1	-0.4	+1.1
Magnesium	(as Mg^{2+})	100	chloride)			
Sodium	(as Na^+)	300	chloride)			
Potassium	(as K^+)	20	chloride)			
Phosphate		5	disodium hydrogen	-0.2	-0.9	+3.5
Silicon		50	sodium silicate	-0.2	+0.7	-1.6
Sulphate		300	hydrogen	-0.5	-0.6	+3.0
Nitrate		100	hydrogen	+0.4	-0.7	+2.9
Fluoride		2	sodium	-0.2	-0.6	-0.2
Anionic Detergent		5		+0.2	+0.3	+1.7

* Determined by the Southern Division, Water Pollution Control Laboratory, Yorkshire Water Authority.

** Determined by the Marine Biological Association, Plymouth.

(e) If other substances did not interfere, the effect would be expected to be (95% confidence) within the ranges.

0.0 \pm 1.1 for 0.0 $\mu\text{g/l}$ Co

0.0 \pm 1.0 for 10.0 $\mu\text{g/l}$ Co

0.0 \pm 0.9 for 50.0 $\mu\text{g/l}$ Co

0.0 \pm 1.0 for 0.0 $\mu\text{g/l}$ Co

0.0 \pm 1.0 for 20.0 $\mu\text{g/l}$ Co for **

0.0 \pm 1.9 for 100.0 $\mu\text{g/l}$ Co

B6 Apparatus

B6.1 An atomic absorption spectrophotometer equipped for an air/acetylene flame and with a cobalt hollow cathode lamp. Facilities for automatic background correction should be used. If the instrument is not equipped with facilities to make this correction, a separate measurement for background must be made, using a suitable continuum. ⁽⁶⁾

B6.2 Cleanliness

Cleanliness is essential for this determination. If possible, apparatus should be reserved solely for cobalt determinations: all residual cobalt from previous cobalt determinations must be removed. Clean all new glass and polyethylene ware by filling with, or soaking in, 10% V/V nitric acid for several hours. 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.

B7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section B6.2 add 2.00 ± 0.05 ml of 50% V/V of hydrochloric acid per litre of sample to be collected, and then collect the sample. Alternatively 1.00 ± 0.05 ml of nitric acid d_{20} (1.42) per litre of sample may be used. The acidification minimizes the adsorption of cobalt onto the walls of the bottle.

B8 Sample Pretreatment

The method described specifies concentration of the sample by evaporation in the presence of nitric acid. This procedure will convert any cobalt present in suspended or colloidal material into a soluble form.

B9 Analytical Procedure

READ SECTION B4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Analysis of samples	
	<i>Pretreatment stage</i> (Carry out this stage in a fume cupboard)	
B9.1	Add 200 ± 1 ml of the sample to a 400-ml borosilicate tall form glass beaker. Add 1.0 ± 0.1 ml of nitric acid (d_{20} 1.42). Cover the beaker with a watch glass and simmer on a hot plate (note a), until the solution volume is reduced to between 5 and 10 ml (note b), and allow to cool.	(a) The hot plate surface temperature should not exceed 160°C , This may be measured by a thermometer standing in a drilled metal block placed on the surface of the hot plate.
B9.2	Cautiously wash down the watch glass and the inside of the beaker with about 10 ml of water and add 1.0 ± 0.1 ml of nitric acid (d_{20} 1.42). Heat gently until the volume of the solution is again reduced to between 5 to 10 ml (note b), and allow to cool.	(b) The 5 to 10 ml volume may be judged by premarking the beaker. It is important to ensure that the liquid does not evaporate to dryness.
B9.3	Transfer the contents of the beaker to a 20-ml calibrated flask. Wash the inside of the beaker with small volumes of water. Add the washings to the contents of the calibrated flask, dilute with water to the mark, stopper and mix thoroughly. Complete the atomic absorption stage during the same working day.	

Step	Experimental Procedure	Notes
	Blank determination	
B9.4	A blank must be run with each batch (eg up to 10 samples) of determinations using the same reagents as for samples. To a 400-ml borosilicate tall form glass beaker, add 200 ± 1 ml of acidified deionized water (note c).	(c) The acidified water is prepared by adding either 2.00 ± 0.05 ml of 50% V/V hydrochloric acid or 1.00 ± 0.05 ml of nitric acid ($d_{20} 1.42$) to 1 litre of water; use the same acid as was used in Section B7.
B9.5	Carry out steps B9.1 to B9.3 inclusive.	
	Calibration standards	
B9.6	Duplicate calibration standards must be run with each batch (eg up to 10 samples) of determinations (see Section B12.4). To a 1-litre calibrated flask add 2.00 ± 0.05 ml of 50% V/V hydrochloric acid, pipette into the flask 5.0 ml of standard cobalt <i>solution B</i> , dilute with water to the mark and mix thoroughly. Transfer 200 ml of this solution to a 400-ml borosilicate tall form glass beaker, and carry out steps B9.1 to B9.3 inclusive.	
	<i>Atomic absorption stage</i>	
B9.7	Set up the instrument, according to the manufacturer's instructions for the determination of cobalt using an air/acetylene flame. The wavelength required is 240.7 nm. Automatic or manual background correction is essential.	
B9.8	Aspirate acidified water (note d) until equilibrium conditions are established. Aspirate one of the calibration standards and adjust the instrument to give a suitable response.	(d) To 100 ± 1 ml of deionized water, add 1.00 ± 0.05 ml of 5M nitric acid.
B9.9	Aspirate acidified water and readjust the zero.	
B9.10	Aspirate the calibration standards with an aspiration of acidified water between each. Let the instrument responses of the calibration standards be C_1 and C_2 .	
B9.11	Aspirate the blank followed by acidified water. Let the instrument response of the blank be B_1 .	
B9.12	Aspirate the samples with an aspiration of acidified water between each. Record the instrument response of the sample. Correct for background and let the corrected response be S .	
B9.13	After each batch of 10 samples re-aspirate the blank and both calibration standards with an aspiration of acidified water in between each. Note the instrument responses of the blank (B_2) and the calibration standards (C_3 and C_4).	

Step	Experimental Procedure	Notes
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Calculation

B9.14

Cobalt concentration =

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

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

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

This calculation assumes a linear calibration curve.
This must be checked (see Section B11).

B10 Measurement of Instrument Responses The instrument responses for samples, standards and blanks are measured with respect to the response of acidified water aspirated on either side (see step B9.8 note d). Most atomic absorption instruments have integration facilities and it is recommended that each sample, standard or blank reading is obtained using a standard fixed integration time (typically 4–10s).

B11 Checking the Linearity of the Calibration Curve The procedure given in this Section must be carried out on at least 2 independent occasions, before application of this method to any samples, and regularly thereafter. Pipette respectively to a series of 1-litre calibrated flasks 0.0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml of standard cobalt solution B, dilute with acidified water (see step B9.4 note c) to the mark, and mix thoroughly. These flasks contain respectively 0, 20, 40, 60, 80 and 100 $\mu\text{g/l}$ cobalt. Carry out the procedure given in Section B9 treating these solutions as if they were samples. Plot the instrument response of each solution against $\mu\text{g/l}$ cobalt. The calibration curve is normally linear; however, the linearity should be checked. If the calibration curve departs from linearity, the calibration standard in step B9.6 may not be appropriate, nor the range given in Section B1.4. In such a case, the calibration standard chosen for step B9.6 should be the highest concentration on the linear portion of the calibration curve, and the concentration range of the method should be amended accordingly.

B12 Change of Concentration Range of the Method If the cobalt concentration of the sample is likely to exceed 100 $\mu\text{g/l}$, an appropriately smaller aliquot of the sample must be taken for analysis, diluted with acidified water (see step B9.4, note c) to 200 ml, and treated as described in the procedure from step B9.1 onwards.

The calculation of the result, step B9.14, must then be altered to

$$\text{Cobalt concentration} = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times \frac{200}{V} \times 100 \mu\text{g/l}$$

where V ml is the volume of sample taken.

Alternatively if the calibration curve is linear beyond 100 $\mu\text{g/l}$ for a particular spectrophotometer the range of the method may be extended up to the extent of linearity of the calibration curve.

B13 Sources of Error The attention which it is necessary to pay sources of error depends on the accuracy required of the analytical results. The following sub-sections summarise the main sources of error:

B13.1 Contamination

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

B13.2 Cobalt content of the water used for blank determinations

If the water used for the blank determinations contains cobalt the results will be falsely low. The importance of this error depends on the cobalt concentration, in both the blank water and the samples. Ideally, the cobalt content of the water used for each blank determination should be measured and an appropriate correction made. An upper limit for the cobalt content of the water can be calculated by converting the instrument response 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 cobalt content of the water.

- (a) To each of two 500 ml borosilicate glass beakers, add 200 ± 1 ml of water and 0.40 ± 0.05 ml of 50% V/V hydrochloric acid or 0.20 ± 0.02 ml of nitric acid ($d_{20} 1.42$); use the same acid as was used in Section B7.
- (b) To each of two 500 ml borosilicate glass beakers, add 400 ± 1 ml of water and 0.40 ± 0.05 ml of 50% V/V hydrochloric acid or 0.20 ± 0.02 ml of nitric acid ($d_{20} 1.42$); use the same acid as was used in Section B7.
- (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 ± 1 ml of water to each beaker from (b) and continue heating until the volumes are reduced to 200 ± 1 ml.
- (d) Analyse the contents of all 4 beakers as described in Section B9, and let the instrument responses be W^1_1 and W^1_2 for the 2 unheated beakers, and W^{11}_1 and W^{11}_2 for the 2 heated beakers.
- (e) The nickel content of the blank water is equivalent to an instrument response of:

$$W = \frac{(W_1^{11} + W_2^{11}) - (W^1_1 + W^1_2)}{4}$$

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

$$A_w = \frac{W}{\bar{C} - \bar{B}} \times 100 \mu\text{g/l cobalt}$$

(See step B9.14)

B13.3 Interfering substances

See Section B3. The effect of possible interfering substances may be determined by analysing water spiked with nickel and various concentrations of the potential interfering substance.

B13.4 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. Therefore, a calibration standard must be run for each batch of analyses, and steps B9.6 onwards give the necessary procedure. This procedure assumes a linear calibration curve and linearity must be checked (see Section B11).

B14 Checking the Accuracy of Analytical Results

Once the method has been put into normal routine operation, many factors may, subsequently, adversely affect the accuracy of the analytical results. It is recommended that experimental tests, to check certain sources of inaccuracy, should be made regularly. Many types of tests are possible, ⁽⁷⁾ and they should be used as appropriate. As a minimum, however, it is suggested that a standard solution of cobalt of suitable concentration be analysed at the same time, and in exactly the same way as normal samples (see step B9.6). 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.

B15 References

- (1) Department of the Environment, File WS/646/50/5, Papers SCA/42/5/7A and B.
- (2) Department of the Environment, File WS/646/50/5, Papers SCA/42/5/8A and B.
- (3) *Copper in Potable Waters by Atomic Absorption Spectrophotometry 1980*, Methods for the Examination of Waters and Associated Materials, HMSO.
- (4) *Zinc in Potable Waters by Atomic Absorption Spectrophotometry 1980*, Methods for the Examination of Waters and Associated Materials, HMSO.
- (5) *Nickel in Potable Waters by Atomic Absorption Spectrophotometry 1981*, Methods for the Examination of Waters and Associated Materials, HMSO.
- (6) *Atomic Absorption Spectrophotometry on Essay Review 1980*, Methods for the Examination of Waters and Associated Materials, HMSO.
- (7) Wilson A L and Cheeseman R V, Water Research Centre, *Technical Report TR6*⁶. Medmenham 1978.

Estimation of the Accuracy of Analytical Results Using the Cobalt Methods

1 Introduction

Quantitative investigation of the accuracy achievable when the cobalt methods are used appears to be limited to work at Yorkshire Water Authority and the Laboratory of the Government Chemist for method A, and Yorkshire Water Authority and the Marine Biological Association for method B. Before firmly recommending the methods 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 these methods, could estimate the accuracy of its own analytical results and report the findings to the Secretary of the Metals and Metalloids Working Group of the DOE/NWC 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 results at zero determinand concentration. The precision of analytical results may depend on the concentration of cobalt 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	Methods A and B
1	Blank†	
2	Another Blank†	
3	Standard solution	10 µg/l Co
4	Standard solution	100 µg/l Co
5	Typical sample	
6	Same sample spiked with	100 µg/l Co

† To be regarded as samples having zero determinand concentration and NOT as true blanks.

It is essential that these solutions be treated exactly as if they were samples and the procedure specified in Section A9 of the method A, and Section B9 of method B, be rigidly followed except that a second true blank should be run with that prescribed in exactly the same manner (ie each of the two true blanks should be analysed in the batch of samples). The six solutions described above should be analysed in random order in with 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. On any one day the same batch of water should be used to prepare these four solutions. For solutions 5 and 6 a total of at least 2 litres of typical sample are required. Prepare solution 6 each day when required by spiking solution 5 as follows; add with a pipette 1.0 ml of standard cobalt solution B (see B5.4.2), to 200 ml of solution 5. When analysing solution 6 it may be necessary to take into account Section A11 or B12 and to take an appropriately smaller aliquot. The total period of the tests may be any convenient time so long as the cobalt

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 cobalt 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 analysis. 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 mean response of the first true blank when performing the conversions for solutions 1, 3, 4, 5 and 6 and deduct the mean response for the second true blank when performing the conversion for solution 2.

3.2 For solutions 3, 4, 5 and 6 calculate the mean concentration of the n results for each solution. For solutions 1 and 2 calculate the overall mean concentration of the 2n results.

3.3 For solutions 3, 4, 5 and 6 calculate the standard deviation, s, of the n results for each solution from:

$$S = \sqrt{\frac{(X_i - \bar{X})^2}{n - 1}}$$

where X_i = the result from the ith batch

\bar{X} = the mean value of X_i .

3.4 Calculate the within-batch standard deviation, S_{wr} , of the results at zero concentration from:

$$S_{wr} = \sqrt{\frac{(X_{1i} - X_{2i})^2}{2n}}$$

where X_{1i} = the result for solution 1 from the ith batch (see 3.1)

X_{2i} = the result for solution 2 from the ith batch (see 3.1)

Note: S_{wr} is not to be confused with the within-batch standard deviation of blank determinations, S_w , from which the limit of detection is often calculated.

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

$$R = \frac{(1.005 \bar{X}_6 - \bar{X}_5)}{100} \times 100 \quad \text{for methods A or B}$$

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	Mean cobalt concentration μg/l	Standard deviation μg/l	Mean recovery %
For methods A or B				
1 and 2 Blanks	2n =			—
3 Standard, 10 μg/l Co	n =			—
4 Standard, 100 μg/l Co	n =			—
5 Sample	n =			—
6 Solution 5 + 100 μg/l Co	n =			

The appropriate sample description should be entered in the space for solution 5. The standard deviation from step 3.4 is entered for the row for solutions 1 and 2 and the standard deviations from step 3.3 are entered for solutions 3 to 6.

* Results to be sent to the following:

The Secretary
The Metals and Metalloids Working Group
The Standing Committee of Analysts
The Department of the Environment
43 Marsham Street
LONDON SW1P 3PY

**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 booklet are requested to write to:

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

Department of the Environment/National Water Council

Standing Committee of Analysts

Members of the Committee responsible for this method:

Dr G I Barrow ¹		Mr W M Lewis ^{1,2}	to 1980
Dr. G A Best ¹	from 1980	Mr P J Long ¹	
Dr G W Bryan ³		Mr G F Lowden ^{2*}	to 1980
Mr W Carr ²		Mr J C McCullins ¹	
Dr J M Carter ¹		Mr P Morries ¹	
Dr G W Clayfield ¹		Mr D Myles ^{1,2}	
Mr B E P Clement ¹		Dr E J Newman ²	
Mr E C Conchie ^{2,3}		Mr A H Nield ¹	
Dr R L Cooper ¹		Dr D I Packham ¹	from 1980
Dr B T Croll ¹		Dr H A Painter ¹	
Mr K G Darrall ³		Mr J F Palframan ²	
Dr J P Day ³		Mr L R Pittwell ¹	
Mr T A Dick ¹		Dr J E Portmann ¹	
Mr J W R Dutton ^{1,2}		Mr L D Purdie ¹	
Mr B J Farey ²	from 1980	Mr B D Ravenscroft ¹	
Mr M G Firth ²	to 1980	Mr B Rhodes ¹	
Dr J Gardiner ^{1,2}	from 1980	Prof J P Riley ^{1,2}	
Mr G I Goodfellow ¹	from 1980	Mr I R Scholes ^{2,3*}	
Mr K Goodhead ¹	to 1980	Mr A Stacey ³	
Mr T R Graham ¹		Mr A Tetlow ¹	from 1980
Mr I Harper ¹		Dr K C Thompson ^{2,3}	
Mr E Hodges ¹		Dr G Topping ²	
Mr G J Holland ¹		Dr A M Ure ¹	from 1980
Dr D T E Hunt ^{1,2}		Mr B T Whitham ¹	
Mr O D Hydes ^{2,3*}		Mr A L Wilson ¹	to 1980
Mr R H Jenkins ²	from 1980		

¹ Members of the Standing Committee

² Members of the Working Group

³ Members of the Panel

* Occasional co-opted member (modifies preceding symbol)

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