Nickel in Potable Waters 1981

Methods for the Examination of Waters and Associated Materials

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Nickel in Potable Waters Tentative Methods (1981 Version)

Methods for the Examination of Waters and Associated Materials

Three methods for the determination of nickel 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 dithiocarbamato-nickel into 4-methylpentan-2-one followed by atomic absorption spectrophotometry. The second, Method B, is based on the spectrophotometric measurement of the coloured complex between nickel and furil-α-dioxime. The third, Method C, 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.

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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.

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

T A DICK
Chairman

L R PITTWELL
Secretary

25 September 1981

A. Nickel in Potable Waters by Atomic Absorption Spectrophotometry Tentative Method (1981 Version)

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.)

Note: Throughout this method nickel is expressed as the element (Ni)

A1.1	Substance determined	All forms of nickel 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 dithiocarbamato – nickel 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*	Nickel concentration (µg/l)	Standard deviation (µg/l)	Degrees of freedom
	A1.6.1 total (a)	0	0.87	23
		5	0.90	44
		50	2.23	34
		80	2.93	44
		100	2.76	23
	A1.6.2 within batch (b)	0	0.92	11
		100	3.30	11
A1.7	Limit of detection (b)	4.3 µg/l with 11 degrees of freedom.		
A1.8	Sensitivity (b)	100 µg/l gives an absorbance of approximately 0.21.		
A1.9	Bias	Not known.		
A1.10	Interferences	See Section A3.		
A1.11	Time required for (a) (b) analysis	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 nickel 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 nickel concentration.

* These data were obtained using this method but without the pre-treatment procedure and without the addition of perchloric acid at step A9.3.

A2 Principle

A2.1 The method described is based on the reaction of nickel with ammonium pyrrolidine dithiocarbamate (APDC) to form a nickel chelate which is extracted into 4- methylpentan-2-one (methyl isobutyl ketone — MIBK). The amount of nickel 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 nickel to forms capable of reacting with APDC.

A2.3 Other elements, for example lead[3], cadmium[4] and cobalt[5] are extracted quantitatively together with nickel 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 nickel by this method is shown in Table A1.

A3.2 The presence of manganese causes low recoveries of nickel and this can be overcome by the addition of perchloric acid to the sample prior to carrying out the solvent extraction stage. The presence of high concentrations of copper (greater than 1 mg/l) also causes low recoveries of nickel. When such high levels of copper are present a precipitate is evident during extraction which remains on the sides of the separating funnel after extraction is complete. The nickel can be recovered (approximately 98%) by extracting the precipitate with a second 10 ml aliquot of MIBK and running this aliquot of MIBK separately through the atomic absorption procedure and adding the nickel found to that present in the original MIBK extract. The presence of high concentrations of detergents (greater than 1 mg/l) also cause low recoveries of nickel but such concentrations are very unlikely to be present in potable waters.

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 nickel 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.

Table A1

Other Substance	Other Substance added as	Concentration of Other Substance mg/l	Effect in µg/l Ni of other substances at a nickel concentration of (d)		
			0 µg/l (a)	50 µg/l (a)	100 µg/l (b)
Zinc (as Zn^{2+})	nitrate	1.0			+ 7.0
,,	,,	5.0	0.3	− 0.6	− 4.3
Iron (as Fe^{3+})	perchlorate	2.0		+ 4.2	− 0.6
,,	,,	5.0	1.9	+ 0.9	− 2.3
Copper (as Cu^{2+})	perchlorate	1.0	0.3	+ 2.8	− 3.0
,,	,,	2.0	1.0	−23.1	−62.2 (e)
,,	,,	5.0	1.3	−40.9	−67.7 (e)

Other Substance	Other Substance added as	Concentration of Other Substance mg/l	Effect in µg/l Ni of other substances at a nickel concentration of (d)		
			0 µg/l (a)	50 µg/l (a)	100 µg/l (b)
Manganese (as Mn^{2+})	nitrate	0.1			−13.5 (f)
,,	,,	0.5			−32.9 (f)
,,	,,	1.0			−51.7 (f)
,,	perchlorate	0.5		− 1.9	
,,	,,	3.0		− 2.6	
,,	,,	5.0	0.1	− 2.6	
Cobalt (as Co^{2+})	nitrate	5.0	0.7	− 1.3	
Sulphate (as SO_4^{2-})	acid	1000.0	0.1	− 0.1	
					(c)
Magnesium (as Mg^{2+})	chloride	100.0			+ 4.9
Calcium (as Ca^{2+})	chloride	200.0			+ 4.7
Sodium (as Na^{+})	chloride	100.0			+ 0.6
Potassium (as K^{+})	chloride	100.0			− 1.7
Orthophosphate (as PO_4^{3-})	sodium	5.0			− 0.3
,,	,,	20.0			− 0.6
Metasilicate (as SiO_3^{2-})	sodium	5.0			− 0.3
,,	,,	20.0			+ 1.0
Dioctyl sulpho-succinate		0.5			− 4.0
,,		1.0			−12.7
,,		2.0			−32.7
,,		5.0			−57.3
Linear alcohol ethoxylate		1.0			− 8.2
,,		2.0			−30.6
,,		5.0			−67.4
Laboratory glassware cleaning agent		1.0			− 0.3
,,		2.0			+ 0.8
		5.0			+ 0.8

(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 be within the range 0.00 ± 1.12 at 0 µg/l, 0.00 ± 4.12 at 50 µg/l and 0.00 ± 6.05 at 100 µg/l nickel
(e) At these levels of copper a precipitate was evident during extraction.
(f) Addition of perchloric acid at step A9.3 removed this effect and has now been incorporated into the method but the effect of other substances when perchloric acid is present has not been checked.

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 **60% m/m Perchloric acid** (d_{20} 1.54)

A5.9 **Standard nickel solutions**

A5.9.1 *Solution A.* 1 ml contains 1 mg Ni.

Weigh accurately 1.000 ± 0.001 g of pure nickel (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.

A5.9.2 *Solution B.* 1 ml contains 2 μg Ni.

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 nickel hollow cathode lamp.

A6.2 **Special Apparatus**

Glass tubes 20 x 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 nickel determinations: all residual nickel from previous nickel 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 nickel 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 nickel to an extractable form. A few organic nickel 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	
	Pretreatment stage (note a)	
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).
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.	
	Solvent extraction stage	
A9.3	Add 0.5 ± 0.1 ml of 60% m/m perchloric acid and 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, cobalt, 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 min ± 15 s. Allow to stand for 5 min ± 30 s and then separate and discard the aqueous phase (note h).	(h) If a precipitate remains in the funnel (see Section A3.2) it should be extracted with a further 10.00 ± 0.05 ml of MIBK, the extract analysed separately and the concentration of nickel found added to that present in the original extract.

Step	Experimental Procedure	Notes
A9.7	Run the organic phase into a sample tube and fit the lid (note i). Complete the atomic absorption stage during the same working day.	(i) All samples, blanks and standards should be processed to this stage before proceeding to the atomic absorption stage.
	Blank determination	
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.	
	Calibration standards	
A10	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 nickel 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.	
	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 232.0 nm.	
A9.13	Aspirate pure MIBK and adjust the zero. Aspirate one of the calibration standards (notes j and k) and adjust the instrument to give a suitable response, eg approximately 80% of full scale deflection.	(j) Keep the aspiration tube above the bottom of the sample tube to avoid aspiration of water which may have collected in the bottom of the sample tube. (k) Do not aspirate more than one-third of the organic phase at this stage as it is required for 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 j) 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 $\bar{B}$.	

Step	Experimental Procedure	Notes

Calculation of results (see Section A11)

A9.17 Calculate the concentration, A, of nickel in the sample from

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

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

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

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 nickel *solution B* and dilute with water to the mark. These flasks contain respectively 0, 20, 40, 60, 80 and 100 µg/l nickel. 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 µg/l nickel.

The calibration curve is normally linear to 100 µg/l nickel, 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 nickel concentration in the sample is likely to exceed 100 µg/l an appropriately smaller aliquot of the sample must be taken for analysis. To this volume of sample, V ml, add sufficient 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:

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

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 source of error.

A12.1 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of nickel 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 nickel 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 Nickel content of the water used for blank determinations

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

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

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

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

(d) Analyse the contents of all four beakers as described in Section A9 and let the measured maximum instrument responses be W^{I}_{1} and W^{I}_{2} for the two unheated beakers and W^{II}_{1} and W^{II}_{2} for the two heated beakers.

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

$$W = \frac{(W_1{}^{II} + W^{II}{}_2) - (W^{I}{}_1 + W^{I}{}_2)}{4}$$

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

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

(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 nickel 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 nickel of suitable concentration be analysed at the same time and in exactly the same way as normal samples (see Section A5.9.2 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/42/5/1A to 1D.

(2) Department of the Environment, File WS/646/50, Papers SCA/42/5/2A to 2C.

(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) *Cobalt in Potable Waters by Atomic Absorption Spectrophotometry 1981.* Methods for the Examination of Waters and Associated Materials, HMSO, 1982.

(6) Department of the Environment, File WS/646/50, Papers SCA/42/5/3A and B.

B. Nickel in Potable Waters by Spectrophotometry Tentative Method (1981 Version)

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).

Note: Throughout this method nickel is expressed as the element (Ni).

B1.1	Substance determined	All forms of nickel (see Sections B2 and B8).		
B1.2	Type of sample	Potable waters.		
B1.3	Basis of the method	The reaction between nickel and furil-α-dioxime to form a coloured complex which is determined spectrophotometrically.		
B1.4	Range of application (a) (b)	Up to 100 μg/l (see Section B12).		
B1.5	Calibration curve (a) (b)	Linear to at least 100 μg/l at 435 nm (see Section B11).		
B1.6	Standard deviation (d)	Nickel concentration (μg/l)	Standard deviation (μg/l)	Degrees of freedom
	1.6.1 Within batch	0.00 (c)	0.11	9
		0.00 (a)	0.41	4
		10.00 (a)	0.47	4
		100.00 (a)	0.97	4
	1.6.2 Total	0.00 (b)	0.08	15
		1.87 (c)	0.14	19
		9.32 (c)	0.13	19
		10.00 (b)	0.20	17
		46.70 (c)	0.32	19
		100.00 (b)	1.46	17
B1.7	Limit of detection	0.28 μg/l with 19 degrees of freedom (b) to 1.75 μg/l with 4 degrees of freedom (a).		
B1.8	Sensitivity (a) (b)	100 μg/l gives an absorbance of approximately 0.47 using 40-mm cells.		
B1.9	Bias	Not known.		
B1.10	Interferences	Copper, chromium, zinc and iron interfere (see Section B3).		
B1.11	Time required for analysis	The total analytical and operator times are the same. Typical times for 10 samples are 150 minutes excluding any pretreatment time.		

(a) These data were obtained at the Department of Chemistry, University of Manchester (1) using a spectrophotometer with 10-mm cells at 435 nm.

(b) These data were obtained at Messrs Ruddock and Sherratt(2) using a spectrophotometer at 435 nm with 10-mn cells for measurements at 100 μg/l Ni and 40-mm cells for measurements at 0 and 10 μg/l Ni.

(c) These data were obtained at the Central Electricity Research Laboratories (3) using a spectrophotometer at 435 nm with 40-mm cells.

(d) These data were obtained using this method but without the pretreatment procedure (Section B8) and distilled water spiked with the stated nickel concentrations.

B2 Principle

B2.1 The method is based on that developed by the Central Electricity Research Laboratories for determining nickel in boiler feed water. (3)

B2.2 It is based on the spectrophotometric measurement at 435 nm of the coloured complex formed by reaction between nickel and furil-α-dioxime.

B2.3 The method specifies boiling the acidified samples and this should ensure that all forms of nickel are converted to forms capable of reacting with furil-α-dioxime. However, it is possible that some samples may require a more rigorous pretreatment (see Section B8).

B3 Interferences

B3.1 The effect of other substances on the determination of nickel by the method described is shown in table B1. The data were obtained by the Central Electricity Research Laboratories. (3)

B3.2 Of the substances most likely to be present in potable waters copper, zinc and iron interfere. The effect of these substances has been further investigated by the Laboratory of the Government Chemist and Messrs Ruddock and Sherratt (4) and the results are given in table B2. From these investigations it is confirmed that copper seriously interferes and it is recommended that the method should not be applied to samples containing more than 1.0 mg/l copper. Chromium at concentrations greater than 0.1 mg/l also seriously interferes with the method.

Table B1

Other substance		Concentration of other substance (mg/l)	Effect in µg/l Ni of other substance at a nickel concentration of (e) (µg/l)		
			0.0	9.3	93.4
Copper II	(as Cu^{2+})	1.0	2.5	2.0	2.0
,,		0.1	0.3	0.3	0.6
Manganese II	(as Mn^{2+})	1.0	0.0	− 0.1	− 0.9
Zinc II	(as Zn^{2+})	1.0	2.4	0.9	0.4
,,		0.1	0.0	0.2	2.0
Cobalt II	(as Co^{2+})	0.1	− 0.1	0.0	− 0.3
Calcium II	(as Ca^{2+})	10.0	0.1	0.4	–
Magnesium II	(as Mg^{2+})	10.0			
Iron III	(as Fe^{3+})	10.0	0.3	0.2	− 6.5
,,		1.0	0.0	0.1	− 2.9
,,		0.1	− 0.1	− 0.2	− 0.6
Chromium III	(as Cr^{3+})	1.0	− 0.2	− 3.0	− 29.6
,,		0.1	0.0	− 0.3	1.5
Aluminium III	(as Al^{3+})	1.0	0.2	0.0	0.8
Molybdenum VI	(as Mo^{6+})	1.0	0.1	− 0.2	–
Vanadium V	(as V^{5+})	1.0	0.1	0.0	–
Vanadium IV	(as V^{4+})	0.1	− 0.2	0.2	–
Titanium IV	(as Ti^{4+})	0.1	0.2	0.1	0.4
Tungsten VI	(as W^{6+})	0.1			
Tin II	(as Sn^{2+})	0.1			
Silicate	(as SiO_3^{2-})	10.0	− 0.1	0.3	–
Orthophosphate	(as PO_4^{3-})	10.0			
Nitrate	(as NO_3^-)	10.0	0.5	0.4	1.0
Fluoride	(as F^-)	1.0			
Fulvic acid		2.5			
Detergents (f)		6.0			

(e) If the other substances did not interfere, the effect would be expected (95% confidence) to lie within the ranges 0.0 ± 0.4, 0.0 ± 0.4 and 0.0 ± 2.4 µg/l Ni at nickel concentrations of 0.0, 9.3 and 93.4 µg/l respectively.

(f) Seven commercial detergent powders (equal proportions by weight were used); the exact composition of these detergents was not investigated.

Table B2

Other substance (added as Chloride)	Concentration of other substance (mg/l)	Effect in μg/l Ni of other substance at a nickel concentration of (g) (μg/l)	
		0.0	10.0
* Copper II (as Cu^{2+})	0.1	1.8	1.7
,,	0.2	2.0	1.4
,,	0.5	2.4	2.0
,,	1.0	2.5	− 0.5
,,	2.0	4.1	− 3.2
Zinc II (as Zn^{2+})	0.5	0.1	− 0.2
	1.0	0.0	0.2
	2.0	0.2	0.1
	5.0	2.2	− 0.7
Copper II (as Cu^{2+}) + Zinc II (as Zn^{2+})	1.0 + 1.0	1.3	0.1
Copper II (as Cu^{2+}) + Zinc II (as Zn^{2+})	2.0 + 2.0	2.2	− 1.8
Iron (III) (as Fe^{3+})	1.0	0.2	0.1
	10.0	0.6	− 0.6
** Copper II (as Cu^{2+})	0.1	2.2	2.5
	0.25	2.0	1.0
	0.5	2.4	3.0
	0.75	1.8	2.5
	1.0	2.6	− 0.8
	2.0	5.5	− 5.8
	5.0	6.0	− 9.5
Zinc II (as Zn^{2+})	0.5	0.0	− 0.5
	1.0	0.0	0.0
	2.0	0.0	0.0
	5.0	0.0	− 0.9
Iron III (as Fe^{3+})	0.5		− 0.5
	1.0		− 0.4
	1.5		− 0.7
	2.0		− 0.4

* Messrs Ruddock and Sherratt

** Laboratory of the Government Chemist

(g) If the other substances did not interfere, the effect would be expected (95% confidence) to be within the ranges 0.0 ± 0.4 and 0.0 ± 0.9 μg/l Ni at nickel concentrations of 0.0 and 10.0 μg/l respectively.

B4 Hazards

Chloroform (see B5.10) is toxic and inhalation of the vapour and skin contact should be avoided.

B5 Reagents

Analytical reagent grade chemicals are suitable unless otherwise specified. Reagents may be stored in glass or polyethylene bottles unless otherwise specified.

B5.1 Water

The water used for blank determinations and for preparing standard and reagent solutions should have a nickel content that is negligible compared with the smallest concentration to be determined in samples. Distilled water is normally suitable. Check the nickel content of the water used for the blanks as described in Section B13.1 and if necessary, make a correction as described in steps B9.10 to B9.12 and B9.14.

B5.2 **Industrial methylated spirit** (95% V/V ethanol, d_{20} 0.81)

B5.3 **50% V/V Hydrochloric acid**

Dilute 500 ± 10 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder.

B5.3.1 *1% V/V Hydrochloric acid*

Dilute 20 ± 1 ml of 50% V/V hydrochloric acid with water to 1 litre in a measuring cylinder.

B5.4 **10%m/V Sodium hydroxide**

Dissolve 100 ± 1 g of high purity sodium hydroxide pellets in water, cool and dilute with water to 1 litre. The reagent should be stored in a polyethylene bottle.

B5.5 **10 Volume Hydrogen peroxide solution**

Dilute 10 ± 1 ml of 100 volume hydrogen peroxide solution with water to 100 ml in a measuring cylinder. This solution should be freshly prepared each week.

B5.6 **0.5% m/V Phenolphthalein solution**

Dissolve 0.50 ± 0.05 g phenolphthalein in 100 ml of water.

B5.7 **10% m/V Sodium potassium tartrate solution**

Dissolve 25 ± 1 g of sodium potassium tartrate in water and dilute with water to 250 ml in a measuring cylinder. Prepare this reagent freshly each week.

B5.8 **0.15% m/V Furil-α-dioxime solution**

Dissolve 0.75 ± 0.05 g of furil-α-dioxime in industrial methylated spirit and dilute with industrial methylated spirit to 500 ml in a measuring cylinder. Store this reagent in a sealed glass bottle and keep in the dark when not in use. This reagent is stable for at least 8 months when stored under these conditions.

B5.9 **2M Ammonium hydroxide solution**

Dilute ammonium hydroxide solution (d_{20} 0.88) with water so that the molarity of the dilute solution is 2.0 ± 0.1M. Store this reagent in a sealed glass bottle; under these conditions its concentration has been found to change by less than 1% in two weeks.

B5.10 **Chloroform**

B5.11 **Standard Nickel solutions**

B5.11.1 *Solution A.* 1 ml contains 1 mg nickel

Weigh 1.000 ± 0.001 g of pure nickel (rod, foil or wire) and dissolve by warming with a mixture of 5 ± 1 ml of nitric acid (d_{20} 1.42) and 15 ± 1 ml of water. When the nickel has dissolved add 10.0 ± 0.5 ml of hydrochloric acid (d_{20} 1.18) and approximately 100 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 6 months. Alternatively a commercially available standard may be used.

B5.11.2 *Solution B.* 1 ml contains 20 μg nickel

To 20.0 ± 0.2 ml of Solution A add 10.00 ± 0.5 ml of hydrochloric acid (d_{20} 1.18) and dilute with water to 1 litre in a calibrated flask. Store in a polyethylene bottle; this solution is stable for at least 6 months.

B5.11.3 *Solution C.* 1 ml contains 0.4 μg nickel

Dilute 20.0 ± 0.2 ml of Solution B with water to 1 litre in a calibrated flask. Prepare this solution freshly each day as required.

B6 Apparatus

B6.1 **Glassware**

Borosilicate glassware should be used throughout. If possible, apparatus should be reserved solely for nickel determinations. All residual nickel from previous determinations must be removed. Clean all new glass and polyethylene ware by filling with or soaking in 10% V/V nitric acid for 2 days. Rinse thoroughly with water. Thereafter a thorough rinse with water after each determination should suffice.

B6.2 **A spectrophotometer or an absorptiometer** using a narrow band pass optical filter having its maximum transmission at 435 nm and 10 and 40-mm cells.

B7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure given in Section B6.1, add to the empty bottle 20 ± 1 ml of 50% V/V hydrochloric acid per litre of sample to be collected and collect the sample. This acidification minimizes the adsorption of nickel onto the walls of the bottle. The dilution of the sample by the acid must be allowed for when calculating the final result (see step B9.14).

B8 Sample Pretreatment

B8.1 The boiling of the acidified samples (step B9.1) should ensure that all forms of nickel are converted to forms capable of reacting with furil-α-dioxime. However, it is possible that some samples containing organically bound nickel may require more rigorous pretreatment. Experience will indicate to analysts whether a more rigorous pretreatment is required for their particular samples.

B8.2 If a more rigorous pretreatment is required add 1.0 ± 0.1 ml of nitric acid (d_{20} 1.42) to the 200 ± 1 ml of sample in step B9.1. Simmer on a hot plate until the solution volume is reduced to 20 ± 5 ml. Cool and dilute with water to 200 ± 5 ml and proceed with step B9.2. It is recommended that analysts should check their particular water samples by comparing the results obtained by carrying out the procedure in this Section with those obtained by carrying out the procedure in Section B9.

B9 Analytical Procedure

READ SECTION B4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Analysis of samples	
B9.1	Add 200 ± 1 ml of sample into a 500-ml conical flask. Cover the neck of the flask with an inverted 50-ml beaker and heat the flask on a hot plate until the solution boils (notes a and b).	(a) See Section B12 for the concentration range of the method. (b) If pretreatment is required see Section B8.2.
B9.2	Remove the flask from the hot plate, cool and transfer the contents to a 500-ml separating funnel. Wash the flask with two 5 ml portions of water and add the washings to the funnel (note c).	(c) The temperature should now be between 15 and 30°C.
B9.3	Add 4 ± 1 drops of 10 volume hydrogen peroxide solution, 2 or 3 drops of 0.5% m/V phenolphthalein solution and 5.0 ± 0.5 ml of 10% m/V sodium potassium tartrate solution. Swirl to mix.	
B9.4	Add dropwise whilst swirling 2.5M sodium hydroxide solution until the phenolphthalein in the solution turns pink. Then add 1% V/V hydrochloric acid solution dropwise until the pink colour is just discharged.	

Step	Experimental Procedure	Notes
B9.5	Add 5.0 ± 0.1 ml of furil-α-dioxime followed immediately by 25 ± 1 ml of 2M ammonium hydroxide solution and swirl for a few seconds.	
B9.6	Add 15.0 ± 0.5 ml of chloroform and shake gently for a few seconds (note d). Shake vigorously for 60 ± 5 seconds and allow the phases to separate for at least five minutes (note e).	(d) Take care to release any pressure from the funnel. (e) Protect the chloroform extract from direct sunlight.
B9.7	Run a small portion of the chloroform phase through a 90-mm diameter, 20-μm pore size filter paper and discard the filtrate. Pass some of the remaining chloroform layer through the same filter paper into a clean 10-mm cell (note f).	(f) If the nickel concentration is less than 20 μg/l use a 40-mm cell.
B9.8	Meanwhile set up the spectrophotometer (see Section B6.2) according to the manufacturer's instructions. Adjust the zero of the instrument with chloroform in the reference cell. Measure the absorbance (see Section B10) of the sample chloroform extract at 435 nm. Recheck the instrument zero. Let the absorbance of the sample be S (note g).	(g) After measurement discard the contents of the sample cell, rinse well with chloroform and allow to dry before filtering the next extract into the cell.
	Blank determination	
B9.9	A blank must be included with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for samples. Carry out steps B9.1 to B9.8 using 200 ± 1 ml of water and 4.0 ± 0.5 ml of 50% V/V hydrochloric acid instead of the sample. Let the absorbance of the blank be B (note h).	(h) If pretreatment (see Section B8.2) was used the blank must be run through the pretreatment procedure.
	Determination of nickel in the water used for the blank (notes i and j).	(i) This determination is not necessary if the nickel content of the water used for the blank is known or is negligible (see Section B13.1). (j) All reagents must be from the same batches as for samples.
B9.10	Add 200 ± 1 ml of the water into a 500-ml separating funnel and add 400 ± 2 ml of the same water to another 500-ml separating funnel. To each funnel add 4.0 ± 0.5 ml of 50% V/V hydrochloric acid. Carry out steps B9.3 to B9.6 inclusive allowing at least 30 minutes for the phases to separate.	
B9.11	Pass the two chloroform extracts through 90-mm diameter, 20-μm pore size filter papers (previously moistened with a few drops of chloroform so that no excess chloroform remains in the paper or the filter funnel) into 25-ml graduated measuring cylinders. Allow all of the chloroform extracts to drain into the cylinders and measure the volumes of the two extracts. Let these be V_T and V_F for the 200 ml and 400 ml samples of water respectively.	

Step	Experimental Procedure	Notes
B9.12	Measure the absorbances of the extracts in 40-mm cells as described in step B9.8. Let the absorbances for the 200 ml and 400 ml samples of water be A_T and A_F respectively. The absorbance, W, due to the nickel in the 200 ml of water used for the blank determination is given by $W = \frac{V_F}{V_T} (A_F - A_T)$ Determine the concentration of nickel, C_w, in the water from W and the appropriate calibration curve.	
	Calculation of results	
B9.13	Calculate the apparent absorbance, R, due to nickel in the sample from $R = S - B$	
B9.14	Determine the apparent nickel concentration, C_a, in the sample from R and the appropriate calibration curve (see Section B11). Calculate the nickel concentration, C, in the original sample from $C = 1.02 (C_a + C_w)$ µg/l (note k)	(k) The factor 1.02 allows for the dilution of the sample by the acid into which it was collected (see Section B7).

B10 Measurement of Absorbance

The exact instrument setting for the wavelength of the absorption peak must be checked for each instrument and then used in all future work. The procedure used for measuring absorbance should be rigorously controlled to ensure satisfactory precision. The same cells should always be used and should not be interchanged between the reference and sample. They should always be placed in the same position in the cell holder with the same face towards the light source. It is difficult to ensure reproducible alignment of cells with chipped corners, and therefore they should be discarded. Similarly, the slide of the cell holder should be kept scrupulously clean. Before every set of measurements the absorbance of the sample cell should be measured against the reference cell when both are filled with water. This will also enable the true absorbance of the blank to be determined.

B11 Preparation of the Calibration Curve

B11.1 Into a series of separating funnels transfer 200, 195, 190, 180, 170, 160 and 150 ml (all ± 1 ml) of water and then add 0.00, 5.00, 10.00, 20.00, 30.00, 40.00 and 50.00 ml of standard nickel *solution C* respectively. These solutions are equivalent to 0, 10, 20, 40, 60, 80 and 100 µg/l nickel respectively. To each funnel add 4.0 ± 0.5 ml of 50% V/V hydrochloric acid and carry out the procedure given in steps B9.3 to B9.8 inclusive using 10-mm cells. Repeat on at least one other occasion. Subtract the average absorbance of the blank from the average absorbances of the other solutions and plot the corrected absorbances against the concentration of nickel added to give a calibration curve. This calibration curve must be checked at frequent intervals and always when a new batch of furil-α-dioxime is used.

B11.2 For determining nickel in the concentration range 0 to 20 µg/l litre it is recommended that 40-mm cells be used. A separate calibration curve prepared and checked in the same manner as B11.1 is required. Into a series of separating funnels transfer 200, 198, 196, 194, 192 and 190 ml (all ± 1 ml) of water and then add 0.00, 2.00, 4.00, 6.00, 8.00 and 10.00 ml of standard nickel *solution C* respectively. These solutions are equivalent to 0, 4, 8, 12, 16 and 20 µg/l nickel respectively. To each funnel add 4.0 ± 0.5 ml of 50% V/V hydrochloric acid and carry out the procedure given in steps B9.3 to B9.8 inclusive using 40-mm cells.

B11.3 If pretreatment of samples is necessary (see Section B8.2) the calibration curve should be prepared by using the same standards as in either B11.1 or B11.2 but which have been run through the pretreatment procedure.

B11.4 The calibration curve is linear to at least 100 μg/l nickel when measurements are made at 435 nm using a spectrophotometer or to at least 30 μg/l nickel using an absorptiometer fitted with a filter. The sensitivity of the latter is less than that obtained by measuring with a spectrophotometer at 435 nm.

B12 Change of Concentration Range of the Method

For samples containing nickel concentrations greater than 100 μg/l an appropriately smaller volume of sample should be taken. Dilute this volume V ml to 200 ml with water and 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. The nickel concentration is the original sample as given by:

$$C = 1.02 \times \left(\frac{200}{V} C_a + C_w \right)$$

B.13 Sources of Error

The analytical procedure can be applied to a wide range of raw and potable waters and the attention which it is necessary to pay to sources of error depends upon the accuracy required. The total nickel concentration should be verified, if in doubt, by the use of the pretreatment procedure (see Section B8). The following sub-sections describe the main sources of error and how they can be minimized, but each analyst must decide what precautions are appropriate to his particular requirements.

B13.1 Effect of Nickel in the Water Used for Blank Determination

If the water used for the blank determination contains nickel, the blank correction will be falsely large and results for samples falsely low. Again, whether or not a correction is required for this effect depends on the error that can be tolerated and the concentration of nickel in the blank water. If the blank response in μg/l Ni is less than the tolerable level in the blank water no further action is necessary. Otherwise the procedure in steps B9.10 to B9.12 allows a correction to be made when required.

When it is necessary to make a correction, to avoid the need for determining C_w in every case it is convenient to estimate C_w for one large batch of water. This value of C_w may then be used for all subsequent batches of analyses for which the same water is used for the blank.

B13.2 Interfering Substances

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

B14 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 method has been put into normal routine operation many factors may subsequently adversely affect the accuracy of analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many types of tests are possible and they should be used as appropriate. However, as a minimum, it is suggested that a solution of known nickel concentration should be analysed at exactly the same time and in exactly the same way as normal samples. 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, Paper SCA/4.2/5/4.

(2) Department of the Environment file WS/646/50, Paper SCA/4.2/5/5B.

(3) Wilson A L, *Analyst*, 1968, *93*, 83–92.

(4) Department of the Environment file WS/646/50, Papers SCA/4.2/5/5A and 6.

C. Nickel in Potable Waters by Atomic Absorption Spectrophotometry Tentative Method (1981 version)

C1 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).

Note: Throughout this method nickel is expressed as the element Ni.

C1.1	Substance determined	All forms of nickel likely to occur in potable waters (see Sections C2 and C8).
C1.2	Type of sample	Potable waters.
C1.3	Basis of the method	Concentration of the sample by evaporation followed by atomic absorption spectrophotometry.
C1.4	Range of application (a)	Up to 100 μg/l (see Section C12).
C1.5	Calibration Curve (a)	Linear to 100 μg/l (see Section C11).

C1.6 Standard deviation

	Nickel concentration (μg/l)	Standard deviation (μg/l)	Degrees of freedom
C1.6.1 within batch	0.0 (a) (c)	0.78	9
	0.0 (a) (d)	0.51	9
	10.0 (a) (c)	0.98	9
	50.0 (a) (c)	0.85	9
	50.0 (a) (d)	1.49	9
	100.0 (a) (c)	2.03	9
	0.0 (b) (c)	0.35	9
	20.0 (b) (c)	0.70	5
	100.0 (b) (c)	1.00	5
C1.6.2 total	0.0 (a) (c)	0.54	9
	0.0 (a) (d)	0.77	9
	10.0 (a) (c)	0.52	9
	50.0 (a) (d)	0.94	9
	100.0 (a) (c)	1.41	9
	0.0 (b) (c)	0.93	9
	20.0 (b) (c)	0.84	9
	100.0 (b) (c)	1.90	9

C1.7	Limit of detection	1.3(b) to 3.4(a) μg/l each with 9 degrees of freedom.
C1.8	Sensitivity (a)	100 μg/l gives an absorbance of approximately 0.1.
C1.9	Bias	Not known.
C1.10	Interferences	None of the metals commonly present in potable waters cause significant interference at moderate concentrations (see Section C3).

C1.11	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 nickel concentration.
(d) Tap water spiked with the stated nickel concentration.

C2 Principle

Nickel 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 nickel 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 cobalt (5).

C3 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) and (2) and is shown in table C1.

C4 Hazards

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

C5 Reagents

All reagents may be kept in glass or polyethylene bottles (see Section C6.2). Analytical reagent grade chemicals are suitable unless otherwise stated.

C5.1 **Water**

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

C5.2 **50% V/V Hydrochloric acid**

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

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

C5.3.1 *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.

C5.3.2 *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.

Table C1

Other substance		Concentration of other substance (mg/l)	Other substance added as	Effect in μg/l Ni of other substance at a nickel concentration of (e)		
				0.0 μg/l	10.0 μg/l	50.0 μg/l
Calcium	(as Ca^{2+})	200	chloride	− 0.3	− 0.3	− 1.7*
Magnesium	(as Mg^{2+})	20	chloride	− 0.5	+ 0.7	+ 0.7
Sodium	(as Na^{+})	100	chloride	+ 0.8	+ 0.7	+ 0.5
Calcium	(as Ca^{2+})	100	chloride			
Magnesium	(as Mg^{2+})	25	chloride	+ 0.7	− 0.3	− 1.7
Sodium	(as Na^{+})	50	chloride			
Potassium	(as K^{+})	10	chloride			
Copper	(as Cu^{2+})	5	chloride			
Zinc	(as Zn^{2+})	5	chloride	+ 0.08	+ 1.3	+ 1.5
Manganese	(as Mn^{2+})	5	chloride			
Iron	(as Fe^{3+})	5	chloride	− 0.1	+ 0.6	+ 0.5
Sulphate	(as SO_4^{2-})	200	hydrogen	+ 0.3	+ 0.3	+ 1.2
Phosphate	(as PO_4^{3-})	20	ammonium dihydrogen	+ 0.6	+ 1.3	+ 2.8
Silicon	(as SiO_2)	20	sodium silicofluoride	+ 1.1	+ 1.1	+ 1.5
Nonionic detergent		10	—	+ 1.4	+ 1.7	+ 2.2
				0.0 μg/l	20.0 μg/l	100.0 μg/l **
Aluminium	(as Al^{3+})	1	nitrate			
Copper	(as Cu^{2+})	5	nitrate			
Iron	(as Fe^{3+})	2	nitrate	− 0.7	+ 0.2	+ 2.1
Manganese	(as Mn^{2+})	2	nitrate			
Zinc	(as Zn^{2+})	5	nitrate			
Calcium	(as Ca^{2+})	300	chloride			
Magnesium	(as Mg^{2+})	100	chloride			
Sodium	(as Na^{+})	300	chloride	+ 0.8	− 0.6	− 0.1
Potassium	(as K^{+})	20	chloride			
Phosphate	(as PO_4^{3-})	5	disodium hydrogen	− 0.5	− 1.4	+ 3.3
Silicon	(as SiO_2)	40	sodium silicate	− 1.5	− 0.7	0.0
Sulphate	(as SO_4^{2-})	300	hydrogen	+ 0.2	− 0.7	− 0.1
Nitrate	(as NO^{3-})	100	hydrogen	− 0.6	− 1.3	− 2.1
Fluoride	(as F^{-})	2	sodium	− 0.2	− 0.3	− 0.2
Anionic detergent		5	—	+ 0.4	− 0.1	0.0

* Determined by Southern Division Water Pollution Control Laboratory, Yorkshire Water Authority.
**Determined by Marine Biological Association, Plymouth.

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

0.0 ± 1.1 at 0.0 μg/l Ni
0.0 ± 1.8 at 10.0 μg/l Ni for * and
0.0 ± 1.1 at 50.0 μg/l Ni

0.0 ± 1.9 at 0.0 μg/Ni
0.0 ± 1.7 at 200.0 μg/Ni for **
0.0 ± 2.7 at 100.0 μg/Ni

C5.4 **Standard nickel solutions**

C5.4.1 *Solution A.* 1 ml contains 1 mg Ni

Weigh 1.000 ± 0.005 g of nickel foil (greater than 99.9% purity), and dissolve it in a mixture of 65 ± 2 ml of nitric acid (d_{20} 1.42) and approximately 65 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 nickel solution.

C5.4.2 *Solution B.* 1 ml contains 20 μg Ni

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.

C6 Apparatus

C6.1 **An atomic absorption spectrophotometer** equipped for an air/acetylene flame and with a nickel 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)

C6.2 **Cleanliness**

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

C7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section C6.2, 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 nickel onto the walls of the bottle.

C8 Sample Pretreatment

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

C9 Analytical Procedure

READ SECTION C4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Analysis of samples	
	Pretreatment stage (Carry out this stage in a fume cupboard)	
C9.1	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 to 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.
C9.2	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.
C9.3	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	
C9.4	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 C7.
C9.5	Carry out steps C9.1 to C9.3 inclusive.	
	Calibration standards	
C9.6	Duplicate calibration standards must be run with each batch (eg up to 10 samples) of determinations (see Section C12.4). To a 1–litre calibrated flask add 2.0 ± 0.1 ml of 50% V/V hydrochloric acid, pipette into the flask 5.0 ml of standard nickel *solution B*, 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 C9.1 to C9.3 inclusive.	
	Atomic absorption stage	
C9.7	Set up the instrument, according to the manufacturer's instructions for the determination of nickel, using an air/acetylene flame. The wavelength required is 232.0 nm. Automatic or manual background correction is essential.	
C9.8	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.
C9.9	Aspirate acidified water and readjust the zero.	
C9.10	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.	
C9.11	Aspirate the blank followed by acidified water. Let the instrument response of the blank be B_1.	
C9.12	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.	
C9.13	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).	
	Calculation	
C9.14	Nickel concentration = $\frac{S-\bar{B}}{\bar{C}-\bar{B}} \times 100\ \mu g/l$ where $\bar{B} = \frac{B_1 + B_2}{2}$ and $\bar{C} = \frac{C_1 + C_2 + C_3 + C_4}{4}$ This calibration assumes a linear calibration curve. This must be checked (see Section C11).	

C10 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 C9.8 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).

C11 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 nickel solution B, dilute with acidified water (see step C9.4 note c) to the mark, and mix thoroughly. These flasks contain respectively 0, 20, 40, 60, 80 and 100 μg/l nickel. Carry out the procedure given in Section C9 treating these solutions as if they were samples. Plot the instrument response of each solution against μg/l nickel. The calibration curve is normally linear; however, the linearity should be checked. If the calibration curve departs from linearity, the calibration standard in step C9.6 may not be appropriate, nor the range given in Section C1.4. In such a case, the calibration standard chosen for step C9.6 should be the highest concentration on the linear portion of the calibration curve, and the concentration range of the method should be amended accordingly.

C12 Change of Concentration Range of the Method

If the nickel concentration of the sample is likely to exceed 100 μg/l, an appropriately smaller aliquot of the sample must be taken for analysis, diluted with acidified water (see step C9.4, note c) to 200 ml, and treated as described in the procedure from step C9.1 onwards.

The calculation of the result, step C9.14, must then be altered to

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

where V ml is the volume of sample taken.

Alternatively if the calibration curve is linear beyond 100 μg/l for a particular spectrophotometer the range of the method may be extended up to the extent of linearity of the calibration curve.

C13 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:

C13.1 Contamination

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

C13.2 Nickel content of the water used for blank determinations

If the water used for the blank determinations contains nickel, the results will be falsely low. The importance of this error depends on the nickel concentration, in both the blank water and the samples. Ideally, the nickel content of the water used for each blank determination should be measured and an appropriate correction made. An upper limit for the nickel 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 nickel 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 C7.

(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 C7.

(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 C9, 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 nickel, A_w in the blank water is then given by

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

(See step C9.14)

C13.3 Interfering substances

See Section C3. The effect of possible interfering substances may be determined by analysing water spiked with nickel and various concentrations of the potential interfering substances.

C13.4 Calibration standards

The calibration curve for this method has been found to be linear, though its slope may vary from one set of determinations to another. Therefore, a calibration standard must be run for each batch of analyses, and steps C9.6 onwards give the necessary procedure. This procedure assumes a linear calibration curve and linearity must be checked (see Section C11).

C14 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 nickel of suitable concentration be analysed at the same time, and in exactly the same way as normal samples (see step C9.6). 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.

C15 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) *Cobalt in Potable Waters by Atomic Absorption Spectrophotometry 1981.* Methods for the Examination of Waters and Associated Materials, HMSO.

(6) *Atomic Absorption Spectrophotometry – An Essay Review 1980.* Methods for the Examination of Waters and Associated Materials, HMSO.

(7) Wilson AL and Cheeseman RV, Water Research Centre, *Technical Report* TR 66, Medmendam 1978.

Appendix

Estimation of the Accuracy of Analytical Results using the Nickel Methods

1 Introduction

Quantitative investigation of the accuracy achievable when the nickel methods are used appears to be limited to work at Yorkshire Water Authority and the Laboratory of the Government Chemist for method A, Messrs Ruddock and Sherratt and the University of Manchester for method B and Yorkshire Water Authority and the Marine Biological Association for method C. 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 nickel 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, B and C
1	Blank**	
2	Another blank**	
3	Standard solution	10 µg/l Ni
4	Standard solution	100 µg/l Ni
5	Typical sample	
6	Same sample spiked with	100 µg/l Ni

** 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, Section B9 of method B, and Section C9 of method C 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 nickel solution B (see B5.11.2), to 200 ml of solution 5. When analysing solution 6 it may be necessary to take into account Section A11 or B12 or C12 and to take an appropriately smaller aliquot. The total period of the tests may be any convenient time so long as the nickel 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 nickel 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 2 n 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 nickel in solution 6 from:

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

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 nickel concentration µg/l	Standard deviation µg/l	Mean recovery %
For methods A, B or C				
1 and 2 Blanks	2n =			–
3 Standard, 10 µg/l Ni	n =			–
4 Standard, 100 µg/l Ni	n =			–
5 Sample	n =			–
6 Solution 5 + 100 µg/l Ni	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 Analysis
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:

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The Department of the Environment
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