

Silver in Waters, Sewages and Effluents

by Atomic Absorption Spectrophotometry 1982

Methods for the Examination of Waters and Associated Materials

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Tentative Methods (1982 Version)

Methods for the Examination of Waters and Associated Materials

Two methods for the determination of silver are described in order to cater for the range of concentrations found in different types of sample. Both methods are based on pretreatment with alkaline iodine and cyanide followed by atomic absorption spectrophotometry. The first, method A, is suitable for use with potable waters and the second, method B, is suitable for use with sewages and sewage/trade effluents.

Contents

Warning to users	2		
About this series	3		
A Silver in Potable Waters	4	B Silver in Sewages and Sewage/Trade Effluents	11
A1 Performance Characteristics of the Method	4	B1 Performance Characteristics of the Method	11
A2 Principle	5	B2 Principle	12
A3 Interferences	5	B3 Interferences	12
A4 Hazards	5	B4 Hazards	12
A5 Reagents	5	B5 Reagents	12
A6 Apparatus	6	B6 Apparatus	13
A7 Sample Collection	7	B7 Sample Collection	13
A8 Sample Pretreatment	7	B8 Sample Pretreatment	13
A9 Analytical Procedure	7	B9 Analytical Procedure	14
A10 Preparation of Calibration Standards	9	B10 Preparation of Calibration Standards	14
A11 Change of Concentration Range of the Method	9	B11 Change of Concentration Range of the Method	15
A12 Sources of Error	9	B12 Sources of Error	15
A13 Checking the Accuracy of Analytical Results	10	B13 Checking the Accuracy of Analytical Results	15
A14 References	10	B14 References	15
Appendix — Estimation of the accuracy of analytical results using the silver methods			16
Address for correspondence			18
Membership responsible for this method			19

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 specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

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, have issued volumes of methods for the analysis of water and sewage culminating in '*Analysis of Raw, Potable and Waste Waters*'. These volumes 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 for Quality Control of the Water Cycle). The Standing Committee of

Analysts is one of the joint technical committees of the Department of the Environment and the national Water Council. It has seven Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

- 1.0 General principles of sampling and accuracy of results
- 3.0 Empirical and physical methods
- 4.0 Metals and metalloids
- 5.0 General non-metallic substances
- 6.0 Organic impurities
- 7.0 Biological methods
- 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

30 November 1982

Silver in Potable Waters by Atomic Absorption Spectrophotometry

Tentative Method 1982 Version

Note: Throughout this method silver is expressed as the element Ag.

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 silver likely to occur in potable waters (see Sections A2 and A8).		
A1.2	Type of sample	Potable waters.		
A1.3	Basis of the method	Pretreatment with alkaline iodine and cyanide to convert silver to stable soluble forms followed by atomic absorption spectrophotometry.		
A1.4	Range of application (a)	Up to 50 $\mu\text{g/l}$		
A1.5	Calibration curve (a)	Slightly curved up to 50 $\mu\text{g/l}$		
A1.6	Standard deviation (a) (within batch)	Silver concentration ($\mu\text{g/l}$)	Standard deviation ($\mu\text{g/l}$)	
		0.0 (b)	0.2 to 0.3	
		5.0 (b)	0.4 to 0.7	
		50.0 (b)	1.7 to 2.0	
		0.0 (c)	0.3 to 0.5	
		5.0 (c)	0.5 to 0.7	
		50.0 (c)	0.9 to 1.3	
(each estimate has 5 degrees of freedom).				
A1.7	Limit of detection (a)	1.2 to 1.7 $\mu\text{g/l}$ (d) 1.7 to 2.8 $\mu\text{g/l}$ (e) (each estimate has 5 degrees of freedom).		
A1.8	Sensitivity (a)	10 $\mu\text{g/l}$ gives an absorbance of approximately 0.02		
A1.9	Bias (a)	Silver concentration ($\mu\text{g/l}$)	Average bias ($\mu\text{g/l}$)	No of analyses
		5.0 (b)	+ 0.18	24
		50.0 (b)	+ 0.40	30
		5.0 (c)	+ 0.04	27
		50.0 (c)	+ 0.19	24
		No important sources of bias have been disclosed by these recovery tests; however, such tests are not able to detect all sources of bias. See Section A2.3 about sample stability.		
A1.10	Interferences	See Section A3. None of the substances tested caused important effects.		
A1.11	Time required for analysis (a)	The total and operator times for a batch of 12 samples are 8 and 5.5 hours respectively.		

(a) These data are based on collaborative tests involving 3 laboratories: BDH Chemicals Ltd, Hopkin and Williams Ltd and Yorkshire Water Authority, Southern Division (1)

(b) Deionized water spiked with the stated silver concentration.

(c) Tap water spiked with the stated silver concentration.

(d) Values obtained by using deionized water.

(e) Values obtained by using tap waters; the waters used contained between 80 and 110 mg/l calcium.

A2 Principle

A2.1 The principle of the method was first described by Owerbach (2) for effluent analysis and has since been used by other workers (3) (4). The sample is treated with iodine and cyanide in alkaline solution to convert any silver present in adsorbed, colloidal or suspended forms into soluble forms. EDTA is added to inhibit the precipitation of other metals, thus minimizing losses of silver by co-precipitation. The determination of silver is completed by atomic absorption spectrophotometry.

A2.2 The method described here is based on work carried out by four collaborating laboratories. In order to apply Owerbach's method to potable waters it was necessary to increase the sensitivity and lower the limit of detection of the method. This was achieved by evaporation to concentrate the solution ten times and by modification of the reagents employed to reduce non-atomic absorption significantly.

A2.3 The effectiveness of the alkaline iodine and cyanide reagent in preventing adsorption losses of silver and in stabilising silver in solution in the sample, when the sample was collected and pretreated as described in Sections A7 and A8, was studied by one of the participating laboratories. Samples of distilled water and tap water were spiked with 3, 20 and 50 $\mu\text{g}/\text{l}$ of silver containing radioactive ^{110}Ag and treated as described in Sections A7 and A8. The radioactivity of each sample was measured at various intervals over a period of 3 weeks. The results showed that at least 90% of silver remained in solution throughout this period (5).

A3 Interferences

The effect of other substances on the determination of silver has been studied by one of the participating laboratories (6). Distilled water spiked with the stated concentrations of silver and other substances was used. None of the other substances tested caused important interference. The results are given in table A1.

A4 Hazards

A4.1 **Potassium cyanide** is used as a reagent in this method (see Section A5.5) and extreme care must be taken over the handling and use of this reagent. It can be lethal if swallowed and it is very toxic in contact with the skin. A face mask and gloves must be worn when handling this reagent. Cyanide solutions must never be made acidic because hydrogen cyanide which is very toxic will be liberated. Used cyanide solutions must be destroyed, for example by the addition of excess sodium hypochlorite solution and standing for 24 hours to ensure complete destruction, before being discharged to the laboratory drain. Cyanide antidote kits are commercially available. **BE FAMILIAR WITH THE FIRST AID PROCEDURE BEFORE USING THIS REAGENT.**

A4.2 **The pH of samples should be checked after the addition of the lithium hydroxide and before the addition of any cyanide to ensure that they are alkaline** (see Section A8), in case they have been inadvertently treated with acid. The nebulizer and drainage system of the atomic absorption spectrophotometer must be thoroughly rinsed before use to remove any acids and after use to ensure that no cyanide remains.

A4.3 The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away.

A5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles unless otherwise stated. (See Section A6.2). Analytical reagent grade chemicals or reagents supplied for use in atomic absorption spectrophotometry should be used where available.

A5.1 Water

The water used for blank determinations and for preparing reagent and standard solutions should have a silver content that is negligible, compared with the smallest concentrations to be determined in the samples. (See Section A9.3). Deionized water or water distilled from an all glass apparatus is suitable.

A5.2 5.0% m/V Lithium hydroxide monohydrate.

Dissolve 5.0 ± 0.1 g of lithium hydroxide monohydrate in water and dilute with water to 100 ml in a measuring cylinder. This reagent must be stored in a polyethylene bottle.

A5.3 25% m/V EDTA diammonium salt, dihydrate.

Dissolve 25.0 ± 0.5 g of ethylenediamine tetraacetic acid diammonium salt, dihydrate, in water and dilute with water to 100 ml in a measuring cylinder.

Table A1 Effect of Other Substances

Other substance	Other Substances added as	Concentration of other substance (mg/l)	Effect in $\mu\text{g}/1$ Ag at a silver concentration of (g)	
			5.0 $\mu\text{g}/1$	50.0 $\mu\text{g}/1$
Chloride	(as Cl^-) Hydrochloric acid	500	+ 0.3	+ 0.2
Nitrate	(as NO_3^-) Nitric acid	300	+ 0.4	+ 0.2
Sulphate	(as SO_4^{2-}) Sulphuric acid	300	+ 0.4	- 0.9
Silicate	(as SiO_2) Sodium silicate	30	- 0.2	+ 0.9
Borate	(as B) Boric acid	5	- 0.1	+ 0.1
Phosphate	(as PO_4^{3-}) Phosphoric acid	5	+ 0.4	- 0.7 (h)
Chromate	(as Cr) Potassium	0.1	+ 0.3	+ 0.8
Sodium	(as Na^+) Nitrate	300	+ 0.1	0.0
Calcium	(as Ca^{2+}) Nitrate	300	+ 0.6	+ 0.2 (h)
Zinc	(as Zn^{2+}) Nitrate	20	0.0	+ 0.4
Aluminium	(as Al^{3+}) Nitrate	5	+ 0.6	- 1.1
Copper	(as Cu^{2+}) Nitrate	5	+ 0.4	- 1.0
Iron	(as Fe^{3+}) Nitrate	5	- 0.3	+ 2.0 (i)
Iron	(as Fe^{3+}) Nitrate	50	- 0.1	- 0.3
Lead	(as Pb^{2+}) Nitrate	5	- 0.4	+ 1.3
Chromium	(as Cr^{3+}) Nitrate	0.1	0.0	- 0.3
Phenol		0.1	- 0.6	+ 1.2
Humic acid	Sodium salt	5.0	+ 1.0	+ 1.6
Humic acid	Sodium salt	10.0	- 1.0	- 2.2
Fulvic acid	Sodium salt	5.0	+ 0.9	+ 1.6
Fulvic acid	Sodium salt	10.0	- 0.3	- 0.5
Detergents (j)		0.5	- 1.0	+ 0.1

(g) If the other substances did not interfere the effect would be expected (95% confidence) to lie within the range 0.0 ± 1.0 and $0.0 \pm 2.1 \mu\text{g}/1$ Ag at 5.0 and 50.0 $\mu\text{g}/1$ Ag respectively.

(h) White crystals deposited on evaporation

(i) A brown precipitate was formed on evaporation

(j) A mixture of equal weights of 6 household detergents was used.

A5.4 1% m/V Iodine solution

Dissolve 1.00 ± 0.05 g of iodine and 1.40 ± 0.05 g of lithium iodide monohydrate in a few ml of water and dilute with water to 100 ml in a measuring cylinder.

A5.5 2% m/V Potassium cyanide

THIS SOLUTION IS VERY TOXIC — SEE SECTION A4 ON HAZARDS

Dissolve 2.00 ± 0.05 g of potassium cyanide in water and dilute with water to 100 ml in a measuring cylinder.

A5.6 Standard silver solutions.

A.5.6.1 Solution A 1 ml contains 1 mg Ag

Dissolve 0.787 ± 0.001 g of silver nitrate in water in a 500-ml calibrated flask, add 30 ± 1 ml of nitric acid ($d_{20} 1.42$) and dilute with water to the mark and mix well. Store in a brown bottle in the dark. This solution is stable for at least one year. Alternatively use a commercially available standard solution.

A5.6.2 Solution B 1 ml contains 5 μg Ag.

Transfer 2.50 ± 0.02 ml of *Solution A* to a 500-ml calibrated flask and add 5.0 ± 0.1 ml of 25% m/V EDTA diammonium salt, 11.0 ± 0.1 ml of 5% m/V lithium hydroxide and mix well. Check that the solution is alkaline (pH greater than 11). Then add 2.5 ± 0.1 ml of 1% m/V iodine solution and 2.5 ± 0.1 ml of 2% m/V potassium cyanide and mix well. Dilute with water to the mark and mix well. Prepare this solution freshly before use.

A6 Apparatus

A6.1 An atomic absorption spectrophotometer equipped for an air/acetylene flame and with a silver hollow cathode lamp. The instrument should be equipped with facilities for

scale expansion and for background correction, either automatically or separately using a suitable continuum or line source (eg cadmium 326.1 nm) (7).

A6.2 Cleanliness

Cleanliness is essential for this determination. If possible, apparatus should be reserved solely for silver determinations: all residual silver from previous analyses must be removed. It is known that silver adheres strongly to glass and other surfaces, and any new apparatus and any apparatus that could have come into contact with silver must be cleaned by leaving it filled for several hours with a dilute alkaline iodine/cyanide/EDTA mixture. This mixture is prepared by adding to 1 litre of water 10.0 ± 0.1 ml of 25% m/V EDTA diammonium salt, 22.0 ± 0.1 ml of 5% m/V lithium hydroxide, checking that the solution is alkaline (pH greater than 11) and then adding 5.0 ± 0.1 ml of 1% m/V iodine and 5.0 ± 0.1 ml of 2% m/V potassium cyanide. The soaked apparatus should be thoroughly rinsed with water before use.

A7 Sample Collection

Clean a polyethylene bottle by the procedure described in Section A6.2, and then collect the sample.

NOTE It is important to ensure that no acid is added to the bottle, because, in the laboratory, the sample will be treated with potassium cyanide. The presence of acid would not only invalidate the analysis but could cause hydrogen cyanide, which is very toxic, to be liberated (see Section A.4).

A8 Sample Pretreatment

READ SECTION A4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

The sample in the collection bottle must be treated as soon as possible with alkaline iodine/cyanide/EDTA mixture, to convert any silver present in adsorbed, suspended or colloidal forms into a soluble form. To each litre of sample add 10.0 ± 0.1 ml of 25% m/V EDTA diammonium salt, 22.0 ± 0.1 ml of 5% m/V lithium hydroxide, check that the solution is alkaline (pH greater than 11), and then add 5.0 ± 0.1 ml of 1% m/V iodine solution and 5.0 ± 0.1 ml of 2% m/V potassium cyanide. Mix thoroughly and leave for at least 16 hours before proceeding with Section A9.

A9 Analytical Procedure

READ SECTION A4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
	Analysis of samples	
	<i>Concentration stage</i>	
A9.1	Add 250 ± 1 ml of the pre-treated sample (see Section A8) to a 600-ml tall form borosilicate glass beaker. Cover the beaker with a watch glass and simmer on a hot-plate (note a) until the solution volume is reduced to between 12 and 15 ml (note b), and allow to cool. (note c)	(a) A few anti-bumping granules may be added. These should be cleaned before use to ensure the complete removal of any traces of silver (see Section A6.2). (b) The 12 to 15 ml volume may be judged by premarking the beaker. The liquid must not be allowed to evaporate to a volume less than 10 ml, as this will cause a precipitate to form that does not readily redissolve. (c) The evaporated solution should not stand for longer than 1 hour before proceeding to step A9.2.
A9.2	Transfer the liquid to a 25-ml calibrated flask. Cautiously wash the inside of the watch glass and beaker with small volumes of water and transfer the washings to the calibrated flask. Dilute with water to the mark, stopper and mix thoroughly. Complete the atomic absorption stage during the same working day.	
	<i>Blank determination</i>	
A9.3	A blank must be run with each batch (eg up to 12 samples) of determinations using the same batch of reagents as for samples. Prepare the blank by pre-treating water in the same way as samples (Section A8) and then carrying out steps A9.1 and A9.2.	

Step	Procedure	Notes
	<i>Calibration standards</i>	
A9.4	Prepare a range of standards as directed in Section A10.	
	<i>Wash solution</i>	
A9.5	Prepare a suitable volume of wash solution (note d). Each 50 ml of this solution contains the same quantities of reagents as were used to prepare the calibration standards (see Section A10) except that the silver must be omitted.	(d) The wash solution is aspirated between each sample and each calibration standard to ensure that no traces of silver have been absorbed in the nebulizer burner system.
	<i>Atomic absorption stage</i>	
A9.6	Set up the instrument according to the manufacturer's instructions for the determination of silver, using an air/acetylene flame, scale expansion and background correction (note e). The wavelength required is 328.1 nm.	(e) Background correction must be applied to all the measurements unless the analyst has shown for his particular samples that it is unnecessary.
A9.7	Aspirate the wash solution until equilibrium is established. Aspirate a calibration standard and adjust the instrument to obtain satisfactory response.	
	<i>Testing the wash solution</i>	
A9.8	The wash solution should be tested as follows (note f). Aspirate the wash solution until equilibrium is established. Aspirate water and adjust the instrument to read zero. Aspirate the wash solution and note the instrument response (correcting for background). This response is a measure of the silver content of the reagents.	(f) This tests the silver content of the reagents used. In developing the method, the silver contributed by the reagents corresponded to not more than the equivalent of about $1\ \mu\text{g}/\text{l}$ in the samples. If values are obtained much in excess of this, then the performance characteristics (Section A1) may not apply.
	<i>Testing the blank</i>	
A9.9	Aspirate and wash solution until equilibrium is established and adjust to zero absorbance. Aspirate the blank solution and record the instrument response (note g).	(g) The blank response should be negligible in comparison with the concentrations of interest in the samples.
	<i>Analysis of standards and samples</i>	
A9.10	Aspirate the wash solution and adjust to zero. Aspirate each calibration standard with an aspiration of the wash solution between each and record the instrument responses of the standards.	
A9.11	Aspirate the wash solution and adjust to zero. Aspirate the samples with an aspiration of the wash solution between each and record the instrument responses of the samples.	
A9.12	Aspirate the wash solution and adjust to zero. Aspirate each calibration standard with an aspiration of the wash solution between each and record the instrument responses of the standards.	
A9.13	Graphically, or by some other suitable method, determine the calibration function of the method, from the results obtained in steps A9.10 and A9.12. The relationship between absorbance and amount of silver in μg is required. (Note h)	(h) The procedure described has been applied to a batch of about 12 samples. If a larger batch is tested, it may be advisable to test one or more calibration standards at suitable intervals to correct for any instrument drift.

Step	Procedure	Notes
	Calculation	
A9.14	From the instrument response of a sample measured in step A9.11 and the calibration function calculated in A9.13, determine the amount of silver, Y , in the sample in μg . The concentration of silver, Z , in the sample is given by $Z = Y \times 4.17 \mu\text{g}/\text{l}$. (note j)	(j) The factor 4.17 arises from the pre-treatment of the sample, which dilutes 1000 ml to 1042 ml, so that the 250 ml of pre-treated sample taken for the analysis contains 240 ml of original sample.

A10 Preparation of the Calibration Standards

Pipette respectively into a series of 50-ml calibrated flasks 0.00, 1.00, 2.00, 3.00, 4.00, 5.00 and 6.00 ml (all ± 0.02 ml) of standard silver *solution B* and dilute each with water to about 20 ml. Add 5.0 ± 0.1 ml of 25% m/V EDTA diammonium salt, 11.0 ± 0.1 ml of lithium hydroxide, mix, check that the solution is alkaline (pH greater than 11) and then add 2.5 ± 0.1 ml of 1% m/V iodine and 2.5 ± 0.1 ml of 2% m/V potassium cyanide, dilute with water to the mark and mix thoroughly. These flasks contain respectively 0, 5, 10, 15, 20, 25 and 30 μg silver. Proceed as described in steps A9.10 and A9.12. Plot the instrument response of each solution against μg silver. The calibration curve is very slightly curved.

A11 Change of Concentration Range of the Method

If the silver concentration in the sample is likely to exceed $50 \mu\text{g}/\text{l}$ an appropriately smaller volume, V_1 (between 25 and 250 ml) may be evaporated in step A9.1 and the procedure described in section A9 followed. It is necessary to alter the calculation of the result (step A9.14) by multiplying by $\frac{250}{V_1}$.

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 summarize the main sources of error.

A12.1 Adsorption of silver

The main problems with the determination of silver are the readiness with which it forms insoluble compounds, and can be strongly adsorbed on a wide variety of surfaces. For these reasons, various precautions are taken in the method. The sample is treated with solubilising the stabilising chemicals and set aside for a period to convert silver into a soluble form and maintain it in stable solution. The same reagents are used in the calibration standards to maintain their stability. Several other precautions are taken for the same reasons.

Adsorption of silver could cause both negative and positive errors, depending on the step reached in the determination. Obviously, adsorption of silver from samples would cause low results, and adsorption from standards could cause apparently high values, (though this is less likely, since a range of standards would show erratic values which would immediately be questioned). Less obviously, adsorption in the nebulizer system of the spectrophotometer would cause errors of both kinds; low results could be obtained from solutions suffering adsorption losses, followed by high results when the silver becomes desorbed as the solubilising reagents are passed through the system. For this reason, a wash solution containing these reagents is used throughout the atomic absorption steps to maintain the cleanliness of the system in respect to silver.

Similarly, any silver previously adsorbed onto glassware will be released by the reagent mixture, and each collaborating laboratory became aware of this effect at some stage of the development of the method. For this reason, it has been recommended that these reagents be used to cleanse all laboratory apparatus before the determination of silver (see Section A6.2). Glassware should be reserved, wherever possible, exclusively for the determination of silver.

A12.2 Contamination of the reagents with silver

In the experience of the collaborating laboratories, however, good laboratory water and the reagents used in the method contribute negligible quantities of "blank" silver.

Nevertheless, steps A9.3, A9.8 and A9.9 were introduced to guard against the possibility of contamination by these reagents.

A12.3 Non-atomic absorption

The reagents do, however, contribute nonatomic absorption (NAA) and so background correction is employed. This NAA is possibly the limiting factor of the method. Considerable efforts were made to reduce the NAA signal, and so improve the sensitivity of the method. The reagents used by previous workers^(1,2,3) were replaced, wherever possible, by others that give lower NAA signals.

Finally, the contribution of samples to the NAA signal should be taken into account. This arises mainly from the calcium in the samples. The tap water samples used in developing this method had calcium contents ranging from 80 to 120 mg per litre. If the method is applied to samples with somewhat higher calcium contents, or high sodium contents the performance characteristics reported in Section A1 may not be applicable.

A12.4 Interfering substances

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

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 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 (8). As a minimum, however, it is recommended that a standard solution of silver (at the upper end of the concentration range of interest) should be analysed at the same time, and in exactly the same way as normal samples (see Section A9). The results obtained should 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/646/144, papers SCA/4.4/Ag 8a to 8d.
- (2) Owerbach, D, *J Applied Photographic Eng*, 1978, 4, 22.
- (3) Department of the Environment, File WS/646/144, paper SCA/4.4/Ag 4.
- (4) Department of the Environment, File WS/646/144, paper SCA/44/Ag 2.
- (5) Department of the Environment, File WS/646/144, papers SCA/4.4/Ag 7 and 9.
- (6) Department of the Environment, File WS/646/144, paper SCA/4.4/Ag 11.
- (7) Standing Committee of Analysts, *Atomic Absorption Spectrophotometry – An Essay Review*, HMSO, London, 1980.
- (8) Wilson AL and Cheeseman RV, Water Research Centre, *Technical Report TR66*, 1978.

Silver in Sewages and Sewage/Trade Effluents by Atomic Absorption Spectrophotometry

Tentative Method 1982 Version

Note: Throughout this method silver is expressed as the element Ag.

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 silver likely to occur in sewages and effluents	
B1.2	Type of sample	Sewages and sewage/trade effluents	
B1.3	Basis of the method	Pretreatment with alkaline iodine and cyanide to convert silver to stable soluble forms followed by atomic absorption spectrophotometry.	
B1.4	Range of application	Up to 6 mg/l	
B1.5	Calibration curve	Slightly curved up to 6 mg/l	
B1.6	Standard deviation (with batch)	Silver concentration (mg/l)	Standard deviation (mg/l)
		0.9 (a) (b)	0.020 to 0.022
		5.8 (a) (c)	0.026 to 0.043
		0.1 (d)	0.002
		5.0 (d)	0.092
		(each estimate has 4 degrees of freedom)	
B1.7	Limit of detection (e)	0.02 to 0.03 mg/l (each estimate has 4 degrees of freedom)	
B1.8	Sensitivity (a)	1 mg/l gives an absorbance of approximately 0.15.	
B1.9	Bias (a)	Average bias of — 0.04 mg/l for 30 determinations of 5.00 mg/l of silver added to a trade effluent	
B1.10	Interference	Not known, but see Section B3	
B1.11	Time required for analysis	The pretreatment time involves allowing the sample to stand for 16 h. After that the total analytical and operator times are the same and for a batch of 10 samples are approximately 1 h.	

(a) These performance characteristics were based on collaborative tests involving 4 laboratories, namely BDH Chemicals Ltd, Hopkin and Williams Ltd, Kodak Ltd and Yorkshire Water Authority, Southern Division (1).

(b) A photoprocessing laboratory effluent.

(c) The same effluent spiked with 5.0 mg/l silver.

(d) A chemical works effluent containing less than 0.01 mg/l silver spiked with the stated concentrations of silver. These results were obtained by Hopkin and Williams Ltd(2).

(e) This estimate is based on experience with distilled water spiked with silver and so probably represents the best achievable. The actual value obtainable on an effluent sample will depend on the size of the non-atomic absorption signal that must be subtracted from the absorption signal due to silver.

B2 Principle

B2.1 The method described is based on that described by Owerbach (3) for analysis of silver in photographic trade effluents, but with slight modifications. The sample is treated with iodine and cyanide in alkaline solution to convert any silver present in adsorbed, colloidal or suspended forms into soluble forms. EDTA is added to inhibit the precipitation of other metals, thus minimising losses of silver by co-precipitation. The determination of silver is completed by atomic absorption spectrophotometry.

B2.2 The method is applicable to the analysis of silver in sewage and trade effluents. A crude sewage spiked with 0.5 and 1.0 mg/l silver, allowing 4 hours for equilibration, was tested using this method and the recoveries obtained were 98 and 98.5% respectively. Therefore the method can be applied to crude sewages; however, each analyst should ascertain that silver can be satisfactorily recovered from any particular crude sewage before applying the method on a routine basis.

B3 Interferences

No specific tests on the effect of other substances on the determination of silver by the method described have been made. However, specific tests have been made on a similar method for potable waters (see Section A3) and it is concluded that important interferences are unlikely.

B4 Hazards

B4.1 **Potassium cyanide** is used as a reagent in this method (see Section B5.3) and extreme care must be taken over the handling and use of this reagent. It can be lethal if swallowed and it is very toxic in contact with the skin. A face mask and gloves must be worn when handling this reagent. Cyanide solutions must never be made acidic because hydrogen cyanide which is very toxic will be liberated. Used cyanide solutions must be destroyed, for example by the addition of excess sodium hypochlorite solution and standing for 24 hours to ensure complete destruction, before being discharged to the laboratory drain. Cyanide antidote kits are commercially available. **BE FAMILIAR WITH THE FIRST AID PROCEDURE BEFORE USING THIS REAGENT.**

B4.2 **The pH of samples should be checked before the addition of any cyanide to ensure that they are alkaline** (see Section B8), in case they have been inadvertently treated with acid. The nebulizer and drainage system of the atomic absorption spectrophotometer must be thoroughly rinsed before use to remove any acids and after use to ensure that no cyanide remains.

B4.3 The exhaust fumes from the atomic absorption spectrophotometer are toxic and must be ducted away.

B5 Reagents

All reagents and standard solutions may be kept in glass or polyethylene bottles unless otherwise stated (see Section B6.2). Analytical grade reagents or reagents supplied for use in atomic absorption spectrophotometry should be used.

B5.1 Water

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

B5.2 10% m/V Iodine solution

Dissolve 10.0 ± 0.1 g of iodine and 11.0 ± 0.1 g lithium iodide monohydrate in water and dilute with water to 100 ml in a measuring cylinder.

B5.3 10% m/V Potassium cyanide in lithium hydroxide solution

THIS SOLUTION IS VERY TOXIC — SEE SECTION B4 ON HAZARDS

Dissolve 10.0 ± 0.1 g of lithium hydroxide monohydrate and 10.0 ± 0.1 g of potassium cyanide in water and dilute with water to 100 ml in a measuring cylinder. This reagent must be stored in a polyethylene bottle.

B5.4 25% m/V EDTA diammonium salt, dihydrate

Dissolve 25.0 ± 0.5 g of ethylenediamine tetraacetic acid diammonium salt, dihydrate in water and dilute with water to 100 ml in a measuring cylinder.

B5.5 Standard silver solutions

B5.6.1 Solution A 1 ml contains 1 mg Ag

Dissolve 0.787 ± 0.001 g of silver nitrate in water in a 500-ml calibrated flask, add 30 ± 1 ml of nitric acid (d_{20} 1.42) and dilute with water to the mark and mix well. Store in a brown bottle in the dark. This solution is stable for at least one year. Alternatively a commercially available standard may be used.

B5.6.2 Solution B 1 ml contains 10 µg Ag

Transfer 5.00 ± 0.02 ml of *solution A* to a 500-ml calibrated flask and add 50.0 ± 0.1 ml of 25% m/V EDTA diammonium salt, 2.5 ± 0.1 ml of 10% m/V iodine solution and 5.0 ± 0.1 ml of 10% m/V potassium cyanide in lithium hydroxide solution and then mix thoroughly. Dilute with water to the mark and mix again. This solution is stable for at least 24 hours.

B6 Apparatus

B6.1 An atomic absorption spectrophotometer equipped for an air/acetylene flame and with a silver hollow cathode lamp. The instrument should be equipped with facilities for scale expansion and for background correction, either automatically or separately using a suitable continuum or line source (eg cadmium 326.1 nm) (4).

B6.2 Cleanliness

Cleanliness is essential for this determination. If possible, apparatus should be reserved solely for silver determinations: all residual silver from previous analyses must be removed. It is known that silver adheres strongly to glass and other surfaces, and any new apparatus and any apparatus that could have come into contact with silver must be cleaned by leaving it filled for several hours with a dilute alkaline iodine/cyanide/EDTA mixture. This mixture is prepared by adding to 1 litre of water 10.0 ± 0.1 ml of 25% m/V EDTA diammonium salt, 5.0 ± 0.1 ml of 10% m/V potassium cyanide in lithium hydroxide solution alkaline (pH greater than 11) and then adding 5.0 ± 0.1 ml of 1% m/V iodine. The soaked apparatus should be thoroughly rinsed with water before use.

B7 Sample Collection

Clean a polyethylene bottle by the procedure described in Section B6.2, and then collect the sample.

NOTE It is important to ensure that no acid is added to the bottle, because, in the laboratory, the sample will be treated with potassium cyanide. The presence of acid would not only invalidate the analysis but could cause hydrogen cyanide, which is very toxic, to be liberated (see Section B.4).

B8 Sample Pretreatment

READ SECTION B4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

The sample in the collection bottle must be treated as soon as possible with alkaline iodine/cyanide/EDTA mixture to convert any silver into a soluble form. To each litre of sample add 10.0 ± 0.1 ml of 25% m/V EDTA diammonium salt. Add 5.0 ± 0.1 ml of 10% m/V iodine solution, check the pH to ensure that the solution is alkaline and add 10.0 ± 0.1 ml of 10% m/V potassium cyanide in lithium hydroxide solution. Mix thoroughly and leave for at least 16 hours before proceeding with Section B9.

Step	Procedure	Notes
	Analysis of Samples	
	<i>Calibration standards</i>	
B9.1	Prepare a range of calibration standards as directed in Section B10	
	<i>Wash solution</i>	
B9.2	Prepare a suitable volume of wash solution (note a). Each 50 ml of this solution contains the same quantities of reagents as were used to prepare the calibration standards (see Section B10) except that the silver must be omitted	(a) The wash solution, which is also the blank, is aspirated between each sample, and calibration standard to ensure that no traces of silver have been absorbed in the nebulizer burner system and to set the instrument zero.
	<i>Atomic absorption stage</i>	
B9.3	Set up the atomic absorption spectrophotometer according to the manufacturer's instructions for the determination of silver, using an air/acetylene flame, and background correction (note b). The wavelength required is 328.1 nm.	(b) Background correction should be applied to all measurements unless the analyst has shown for his particular samples that it is unnecessary.
B9.4	Aspirate the wash solution until equilibrium is established and adjust to zero. Aspirate one of the calibration standards and adjust the instrument to get a satisfactory response. Reaspirate the wash solution and, if necessary, readjust the zero.	
B9.5	Aspirate each calibration standard with an aspiration of wash solution between each and record the instrument responses of the standards.	
B9.6	Aspirate the wash solution and, if necessary, readjust the zero. Aspirate the pretreated samples (Section B8) with an aspiration of the wash solution between each and record the instrument responses of the samples.	
B9.7	Repeat step B9.5	
B9.8	Graphically, or by some other suitable method, determine the calibration function of the method from the results obtained in steps B9.5 and B9.7. The relationship between instrument response and the amount of silver in mg is required (note c).	(c) The procedure described has been applied to batches of about 12 samples. If a larger batch is tested it may be advisable to test one or more calibration standards at suitable intervals to test for any instrument drift.
	<i>Calculation of results</i>	
B9.9	From the instrument response of a sample measured in step B9.6 and the calibration function calculated in step B9.8 determine the amount of silver, Y, in the sample in mg/l. The concentration of silver, Z, in the original sample is given by $Z = Y \times 1.025 \text{ mg/l}$ (note d)	(d) The factor of 1.025 allows for the dilution of the sample by the reagents added in Section B8.

B10 Preparation of the Calibration Standards

Pipette respectively into a series of 50-ml calibrated flasks 0.00, 1.00, 2.00, 3.00, 4.00, 5.00, 10.00, 20.00 and 30.00 ml (all ± 0.01 ml) of standard silver solution B and dilute each with water to about 30 ml. Add 0.50 ± 0.02 ml of 25% m/V EDTA diammonium salt, 0.25 ± 0.02 ml of 10% m/V iodine solution, check the pH to ensure that the solution is alkaline, add 0.50 ± 0.02 ml of 10% m/V potassium cyanide in lithium hydroxide solution, dilute with water to the mark and mix thoroughly. These solutions contain respectively 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0 and 6.0 mg/l silver. If the expected concentration of silver in the

samples is less than 1.0 mg/l the first six standards only need be prepared. If the expected concentration of silver in samples is between 1.0 and 6.0 mg/l the last four standards plus the 0.0 mg/l standard only need be prepared. Proceed as described in steps 9.5 and 9.7. Plot the instrument response of each solution against mg silver. The calibration function may be slightly curved.

B11 Change of Concentration Range of the Method

B11.1 If the silver concentration in the sample is likely to exceed 6 mg/l a suitable volume (V_1 ml) of the pretreated sample (Section B8) should be diluted with the wash solution (step B9.2) to V_2 ml, before carrying out the atomic absorption measurement (step B9.6). It is necessary to alter the calculation of the result (step B9.9) by multiplying by $\frac{V_2}{V_1}$.

B12 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.

B12.1 Adsorption of silver

The main problems with the determination of silver are the readiness with which it forms insoluble compounds, and can be strongly adsorbed on a wide variety of surfaces. For these reasons, various precautions are taken in the method. The sample is treated with solubilising and stabilising chemicals and set aside for a period to convert silver into a soluble form and maintain it in stable solution. The same reagents are used in the calibration standards to maintain their stability. Several other precautions are taken for the same reasons.

Adsorption of silver could cause both negative and positive errors, depending on the step reached in the determination. Obviously, adsorption of silver from samples would cause low results, and adsorption from standards could cause apparently high values, (though this is less likely, since a range of standards would show erratic values which would immediately be questioned). Less obviously, adsorption in the nebulizer system of the spectrophotometer would cause errors of both kinds; low results could be obtained from solutions suffering adsorption losses, followed by high results when the silver becomes desorbed as the solubilising reagents are passed through the system. For this reason, a wash solution containing these reagents is used throughout the atomic absorption steps to maintain the cleanliness of the system in respect to silver.

Similarly, any silver previously adsorbed onto glassware will be released by the reagent mixture, and each collaborating laboratory became aware of this effect at some stage of the development of the method. For this reason, it has been recommended that these reagents be used to cleanse all laboratory apparatus before the determination of silver (see Section B6.2). Glassware should be reserved, wherever possible, exclusively for the determination of silver.

B12.2 Interfering substances

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

B13 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 (5). As a minimum, however, it is recommended that a standard solution of silver (at the upper end of the concentration range of interest) should be analysed at the same time, and in exactly the same way as normal samples (see Section B9). The results obtained should 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.

B14 References

- (1) Department of the Environment, File WS/646/144, papers SCA/44/Ag 14A-14C
- (2) Department of the Environment, File WS/646/144, paper SCA/44/Ag 12
- (3) Owerbach D, *J Applied Photographic Eng*, 1978, 4, 22.
- (4) Standing Committee of Analysts, *Atomic Absorption Spectrophotometry - An Essay Review*, HMSO, London, 1980.
- (5) Wilson A L and Cheeseman R V, Water Research Centre, *Technical Report* TR 66, 1978.

Appendix

Estimation of the Accuracy of Analytical Results using the Silver Methods

1 Introduction

Quantitative investigation of the accuracy achievable when the silver methods are used appears to be limited to work at three participating laboratories for method A and four participating laboratories 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 determined concentration. The precision of analytical results may depend on the concentration of silver 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	Method A $\mu\text{g/l Ag}$	Method B mg/l Ag
1	Blank†		
2	Another Blank†		
3	Standard solution	5	1.0
4	Standard solution	50	5.0
5	Typical sample		
6	Same sample spiked with	25	2.5

†To be regarded as samples having zero determined 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 reagents 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 2.5 litres of typical sample are required for method A and 0.5 litres of typical sample are required for method B. Prepare solution 6 each day when required by spiking solution 5 as follows; add with a pipette 1.25 ml of standard silver solution B (see A5.6.2), to 250 ml of solution 5 for method A; add with a pipette 2.5 ml of an intermediate standard silver solution (1 ml contains 100 $\mu\text{g Ag}$ prepared as indicated in B5.6.2 but using 50 ml of solution A) to 100 ml of solution 5 for method B. When analysing solution 6 it may be necessary to take into account Section A11 or B11

and to take an appropriately smaller aliquot. The total period of the tests may be any convenient time so long as the silver 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 silver 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 silver in solution 6 from:

$$R = \frac{(1.005 \bar{X}_6 - \bar{X}_5)}{25} \times 100 \quad \text{for method A}$$

$$\text{or } R = \frac{(1.025 \bar{X}_6 - \bar{X}_5)}{2.5} \times 100 \quad \text{for method B}$$

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 silver concentration	Standard deviation	Mean recovery
For method A		$\mu\text{g}/1$	$\mu\text{g}/1$	%
1 and 2 Blanks	2n =			—
3 Standard, 5 $\mu\text{g}/1$ Ag	n =			—
4 Standard, 50 $\mu\text{g}/1$ Ag	n =			—
5 Sample	n =			—
6 Solution 5 + 25 $\mu\text{g}/1$ Ag	n =			
For method B		$\text{mg}/1$	$\text{mg}/1$	%
1 and 2 Blanks	2n =			—
3 Standard 1.0 $\text{mg}/1$ Ag	n =			—
4 Standard 5.0 $\text{mg}/1$ Ag	n =			—
5 Sample	n =			—
6 Solution 5 + 2.5 $\text{mg}/1$ Ag	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
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