Antimony in Effluents and Raw, Potable and Sea Waters by Spectrophotometry (Using Crystal Violet) 1982 Tentative method

Methods for the Examination of Waters and Associated Materials

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Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in 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 proven 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, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as 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 the 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 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

Antimony in Effluents and Raw, Potable and Sea Waters by Spectrophotometry. Tentative Method (1982 Version)

1 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 antimony is expressed as the element, Sb.

1.1	Substance determined	All forms of antimony (see Section 2.2).
1.2	Type of sample	Effluents and raw, potable and sea waters.
1.3	Basis of the method	Coprecipitation with hydrous zirconium oxide followed by extraction and then determination of the chloroantimonate-crystal violet ion pair by spectrophotometry.
1.4	Range of application (a)	Up to at least 2.0 μg/l.
1.5	Calibration curve (a)	Linear up to at least 2.0 μg/l.

1.6 Standard deviation (within batch) (a).

Antimony concentration (μg/l)	Standard deviation (μg/l)	Degrees of freedom (μg/l)
0.00 (b)	0.003	5
0.50 (b)	0.008	5
0.08 (c)	0.003	5
0.26 (d)	0.003	8
0.76 (e)	0.008	5
2.45 (f)	0.023	5
0.09 (g)	0.002	4
0.07 (h)	0.002	4

1.7	Limit of detection (a)	0.012 μg/l with 6 degrees of freedom
1.8	Sensitivity (a)	0.5 μg/l gives an absorbance of 0.24 with a 1 litre sample.
1.9	Bias (a)	Tests for the recovery of antimony from samples of distilled water, sea water (d) and stripped sea water (i) gave the following results. These disclosed no important sources of bias; however recovery tests do not check all sources of bias.

Antimony	Recovery (μg/l) from		
Concentration added (μg/l)	Distilled Water	Sea Water	Stripped Sea Water
0.00	0.00	0.26	0.00
0.10	0.10	0.36	0.10
0.20	0.20	0.46	0.21
0.50	0.50	0.75	0.50
0.70	0.70	0.96	0.70
1.00	1.00	1.26	1.01

1.10 Interferences (a)	See Section 3. Thallium, oxalate and tartrate showed just significant interference. Fulvic acid showed significant interference but this is overcome by the pre-treatment procedure.
1.11 Time required for analysis (a)	For 6 samples the total analytical time is about 6 hours of which about 4.5 hours are operator time. These times exclude any pre-treatment time.

(a) These data were obtained using 1 litre samples in the Department of Oceanography, University of Liverpool,[1] using a spectrophotometer at 610 nm and a micro-cell of path length 40 mm. Pretreatment was not used.
(b) Distilled water spiked with the stated concentration of antimony.
(c) Water from Lake Celyn.
(d) Water from the Irish Sea.
(e) Water from the Irish Sea spiked with 0.5 μg/l antimony.
(f) Treated sewage effluent (250 ml used) filtered through a glass fibre filter capable of retaining particles greater than 0.7 μm.
(g) Effluent from edible oil refinery filtered as (f)
(h) Effluent from a brine works filtered as (f).
(i) Water from the Irish Sea stripped of antimony by passage through a column packed with alumina.

2 Principle

2.1 The method is based on experimental work carried out at the Department of Oceanography, University of Liverpool.[1]

2.2 After pre-treatment with peroxodisulphate to oxidize organic compounds and to decompose organo-antimony compounds, inorganic antimony (Sb III and Sb V) is coprecipitated with hydrous zirconium oxide at pH 5.0. The precipitate is dissolved in hydrochloric and sulphuric acids. Antimony is reduced to Sb^{3+} in 6M hydrochloric acid solution using titanium (III) chloride. It is then oxidised to Sb^{5+} using sodium nitrite, the excess of which is destroyed by adding urea. After dilution to 0.7M with respect to hydrochloric acid, ethanol and a solution of crystal violet are added. The resultant intensely coloured ion pair is extracted into toluene and the absorbance is measured at 610 nm.

3 Interferences

The effects of potential interfering substances on the determination of antimony by this method are given in Table 1. The majority of these substances are eliminated at the coprecipitation stage. Thallium, oxalate and tartrate show just significant interference at the 0.0 μg/l antimony level. Only fulvic acid shows a significant interference and this can be readily eliminated by carrying out a pre-treatment with peroxodisulphate. This pre-treatment also decomposes organo-antimony compounds.

4 Hazards

4.1 Care is required when handling and preparing solutions of antimony potassium tartrate (Section 5.13) as this compound is toxic. If any is ingested immediately carry out gastric aspiration and lavage and obtain medical attention.

4.2 The addition of sulphuric acid (d_{20}1.84) to water (Section 5.2) is hazardous and must be carried out with great care whilst gently swirling the contents of the flask.

4.3 Toluene is moderately toxic (Section 5.10) (threshold limit value in air is 100 ppm). Short term exposure to concentrations greater than 200 ppm in air may cause dizziness and mental disorders. Extractions using toluene should be carried out in a fume cupboard. Toluene is flammable.

5 Reagents

All reagents and standard solutions should be stored in polyethylene containers which have been cleaned by the procedure described in Section 6.2 unless otherwise stated. Analytical grade reagents should be used unless otherwise specified.

5.1 Water

The water used for the blank determinations and for preparing reagents and standard solutions should have an antimony content which is negligible compared with the smallest concentration to be determined in samples (see Section 12.2). Water distilled from an all glass apparatus has been found to be satisfactory.

Table 1. Effect of other substances on the determination of antimony (a).

Other Substance	Other substances added as	Concentration of other substance (mg/l)	Effect in µg/l Sb of other substances at an antimony concentration of (b). 0.00 µg/l	0.500 µg/l
Sodium (as Na^+)	Chloride	30000	0.000	+0.005
Potassium (as K^+)	Chloride	1000	+0.002	−0.005
Magnesium (as Mg^{2+})	Chloride	1000	−0.005	−0.002
Calcium (as Ca^{2+})	Chloride	1000	0.000	−0.003
Aluminium (as Al^{3+})	Sulphate	10	+0.003	−0.004
Bismuth (as Bi^{3+})	Nitrate	10	+0.002	+0.006
Boron (as B)	Boric Acid	10	+0.002	+0.002
Cadmium (as Cd^{2+})	Sulphate	10	−0.004	0.000
Chromium (as Cr^{3+})	Sulphate	1	+0.002	−0.005
Cobalt (as Co^{2+})	Nitrate	10	0.000	+0.003
Gold (as Au^{3+})	Chloride	0.0004	+0.005	+0.005
Iron (as Fe^{2+})	Sulphate	10	+0.003	+0.006
Iron (as Fe^{3+})	Chloride	10	−0.005	+0.006
Lead (as Pb^{2+})	Nitrate	10	−0.004	+0.004
Manganese (as Mn^{2+})	Sulphate	10	+0.003	+0.006
Mercury (as Hg^{2+})	Chloride	0.5	−0.001	−0.001
Nickel (as Ni^{2+})	Nitrate	10	−0.002	+0.002
Thallium (as Tl^+)	Nitrate	10	+0.010	+0.006
Zinc (as Zn^{2+})	Sulphate	10	+0.005	−0.009
Copper (as Cu^{2+})	Sulphate	10	+0.002	−0.002
Acetate (as $C_2H_3O_2-$)	Sodium	10	+0.005	+0.004
(Arsenic (III) (as As)	Sodium Arsenite	1	+0.004	+0.003
Bromide (as Br^-)	Potassium	10	+0.005	+0.005
Citrate (as $C_6H_5O_7^{3-}$)	Sodium	10	+0.005	+0.005
Cyanide (as CN^-)	Potassium	10	+0.003	+0.004
EDTA (as $C_{10}H_{14}N_2O_8^{2-}$)	Disodium	20	+0.004	−0.003
Fluoride (as F^-)	Sodium	10	+0.005	+0.006
Nitrate (as NO_3^-)	Potassium	10	0.000	0.000
Oxalate (as $C_2O_4^{2-}$)	Ammonium	10	+0.010	+0.008
Phosphate (as PO_4^{3-})	Dipotassium	10	+0.002	+0.003
Sulphate (as SO_4^{2-})	Sodium	2000	+0.001	+0.003
Tartrate (as $C_4H_4O_6^{2-}$)	Tartaric Acid	10	+0.010	+0.009
Thiocyanate (as CNS^-)	Potassium	10	+0.006	+0.006
Thiosulphate (as $S_2O_3^{2-}$)	Sodium	10	+0.008	+0.006
Lauryl Sulphate	Sodium	10	−0.002	+0.004
Cetyl trimethyl ammonium	Bromide	5	+0.003	−0.004
Fulvic Acid	Ammonium	0.3 (c)	+0.002	−0.004
Fulvic Acid	Salt	1 (c)	0.000	−0.095
Fulvic Acid		2 (c)	+0.002	−0.110
Fulvic Acid		10 (d)	−0.004	+0.002

(a) These data were obtained in the Department of Oceonography, University of Liverpool

(b) If the other substance did not interfere the effect would be expected (95% confidence) to lie within the ranges 0.000 ± 0.007 µg/l and 0.000 ± 0.018 µg/l at antimony concentrations of 0.000 and 0.500 µg/l respectively.

(c) Sample not pre-treated

(d) Sample pre-treated using potassium peroxodisulphate.

5.2 **30% V/V Sulphuric acid**

This preparation is hazardous (see section 4.2). Add slowly and cautiously with stirring 300 ± 20 ml of sulphuric acid (d_{20}1.84) to 650 ml of water in a 2-litre beaker which is standing in cold water. When thoroughly mixed and cooled, transfer to a measuring cylinder and dilute with water to 1 litre.

5.3 **Hydrochloric acid** (d_{20}1.18)

5.3.1 **6M Hydrochloric acid** (approximately)

Dilute 260 ± 10 ml of hydrochloric acid (d_{20}1.18) with water to 500 ml in a measuring cylinder.

5.3.2 **7M Hydrochloric acid** (approximately)

Dilute 310 ± 10 ml of hydrochloric acid (d_{20}1.18) with water to 500 ml in a measuring cylinder.

5.4 **6M Ammonia solution** (approximately).

Analytical reagent grade ammonia solution (d_{20}0.880) sometimes contains a significant concentration of antimony. Purify it by placing a polyethylene beaker containing 100 ± 2 ml of it and 200 ± 4 ml of water in a desiccator for 4–5 days. Store the solution in a polyethylene bottle and renew it every two weeks.

5.5 **Zirconyl chloride**

Analytical reagent grade zirconyl chloride is often impure and therefore it should be purified before use. Dissolve 100 ± 3 g of zirconyl chloride octahydrate in 160 ± 10 ml of water and filter the solution through a glass fibre filter paper. Add sufficient hydrochloric acid (d_{20}1.18) to give a total volume of 480 ml. Stir the solution and allow it to stand for at least 1 hour. Collect the precipitate on a glass fibre filter. Dissolve it in the minimum volume of water and reprecipitate by the addition of sufficient hydrochloric acid (d_{20}1.18) to give an acid molarity of 8.5 ± 0.5M. Using suction collect the crystals on a sintered glass filter (porosity 3) transfer them to a clockglass and place them in a desiccator containing sodium hydroxide pellets. After 3 days allow the crystals to dry in the air and then grind them to a fine powder.

5.6 **1.0% m/V Titanium (III) chloride solution**

Dilute 6.7 ± 0.1 ml of 15% m/V titanium (III) chloride solution with 6M hydrochloric acid to 100 ml. Prepare this solution each week.

5.7 **10% m/V Sodium nitrite solution.**

Dissolve 10.0 ± 0.5 g of sodium nitrite in water and dilute with water to 100 ml. This solution is stable for at least one year.

5.8 **50% m/V Urea solution**

Dissolve 50 ± 1 g of urea in the minimum volume of water and dilute with water to 100 ml. This solution is stable for at least one year.

5.9 **0.1% m/V Crystal violet solution**

Dissolve 100 ± 3 mg of crystal violet in 100 ml of water. This solution is stable for at least one month if stored in the dark.

5.10 **Toluene**

This reagent is hazardous (see Section 4.3)

5.11 **Ethanol** (absolute)

5.12 **Potassium peroxodisulphate**

5.13 **Standard antimony solutions**

These solutions are hazardous (see Section 4.1)

5.13.1 *Solution A.* 1 ml contains 100 μg Sb.

Dissolve 0.1334 ± 0.0003 g of antimony potassium tartrate (dried at 105 ± 5° C) in water and dilute with water to 500 ml in a calibrated flask. Store the solution in a well stoppered glass bottle. It is stable for at least one year.

5.13.2 *Solution B.* 1 ml contains 1 μg Sb.

Dilute 10.00 ± 0.02 ml of Solution A with water to 1 litre in a calibrated flask. This solution should be freshly prepared before use.

5.13.3 *Solution C.* 1 ml contains 0.1 μg Sb.

Dilute 10.00 ± 0.02 ml of Solution B with water to 100 ml in a calibrated flask.

6 Apparatus

6.1 **A spectrophotometer** of prism or grating type fitted with micro-cells of 40 mm path length and a capacity of not greater than 1.5 ml.

6.2 **Cleanliness**

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

7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section 6.2 add 3.0 ± 0.1 ml of 6M hydrochloric acid per litre of sample to be collected and then collect the sample. Waters of this acidity (approximately 0.02M) can be stored for at least seven days in polyethylene bottles without significant change.

8 Analytical Procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Procedure	Notes
	Pre-treatment stage.	
	This pre-treatment should be carried out on all samples unless the analyst from knowledge and experience of his particular waters and confirmation by testing has shown it to be unnecessary (note a)	(a) If treatment is not required start at step 8.2
8.1	Place 1.00 ± 0.01 litre of the acidified sample (see section 7) in a 2-litre conical flask and add 350 ± 50 mg of potassium peroxodisulphate. Heat the solution to 80 ± 5° C for 1 to 1.5 hours on a hot plate then cool to room temperature. Proceed to step 8.2 beginning with the addition of the zirconyl chloride.	

Step	Procedure	Notes
	Determination of Antimony	
8.2	Place 1.00 ± 0.01 litre of the acidified sample or pre-treated sample in a 2-litre conical flask. Add 150 ± 10 mg of zirconyl chloride and stir the solution mechanically until dissolution is complete. While continuing to stir gradually add 6M ammonia solution until a pH of 5.0 ± 0.3 is attained. Remove the stirrer from the solution and rinse it with a little water.	
8.3	Allow the precipitate to settle for at least 1.5 hours (note b). Decant the supernatant liquid through a 7 cm glass fibre filter (capable of retaining particles greater than 1 μm) using suction. Wash the precipitate by decantation using 150 ± 10 ml of hot (approximately 70° C) water, passing the washings through the filter. Transfer the precipitate to the filter using 100 ± 10 ml of hot (approximately 70° C) water. Reject the filtrate.	(b) Up to 48 hours is not detrimental.
8.4	Dissolve the precipitate on the filter using successively 8.0 ± 0.1 ml and 7.0 ± 0.1 ml of 7M hydrochloric acid and 3.0 ± 0.1 ml of 30% V/V sulphuric acid. Rinse the walls of the flask with 4.0 ± 0.1 ml of 7M hydrochloric acid and transfer to the filter. Finally wash the filter with a further 5.0 ± 0.1 ml of 7M hydrochloric acid. Collect the various acid filtrates in a 250-ml separating funnel.	
8.5	To the combined filtrates add 1.0 ± 0.1 ml of 1% m/V titanium (III) chloride solution, mix and allow to stand for 1.5 ± 0.5 min. Add 1.5 ± 0.1 ml of 10% m/V sodium nitrite solution, mix and allow to stand for 4 ± 1 min. Add 2.0 ± 0.1 ml of 50% m/V urea solution, mix and allow to stand for 2.0 ± 0.5 min. Add a mixture of 180 ± 5 ml of water and 10 ± 1 ml of ethanol, mix and add 1.00 ± 0.05 ml of 0.1% m/V crystal violet solution.	
8.6	With a safety pipette add 3.00 ± 0.02 ml of toluene and extract for 1.25 ± 0.25 min. Allow the phases to separate and run off and discard the lower layer. Dry the stem of the separating funnel with a strip of filter paper. Run the organic phase into a 10 ml centrifuge tube, stopper and centrifuge for 1.0 ± 0.1 min at 500 G. (note c).	(c) A flameproof centrifuge must be used.
8.7	Measure the absorbance of the centrifugate at 610 nm in a 40 mm micro-cell againt toluene in the reference micro-cell. Let the absorbance of the sample be S.	
	Blank Determination	
8.8	A blank determination must be carried out with each batch of samples in an identical manner to that used for samples. To 1.00 ± 0.01 litre of water in a 2 litre conical flask add 3.0 ± 0.1 ml of 6M hydrochloric acid. If pre-treatment was used carry out steps 8.1 to 8.7 inclusive; if pre-treatment was not used carry out steps 8.2 to 8.7 inclusive. Let the absorbance of the blank be B.	

Step	Procedure	Notes
	Calibration Standards	
8.9	A duplicate calibration standard must be run with each batch of samples in an identical manner to that used for samples. Add 10.00 ± 0.02 ml of standard antimony solution C to 1.00 ± 0.01 litre of water in a 2 litre conical flask. (This corresponds to 1 μg/l Sb). Add 3.0 ± 0.1 ml of 6M hydrochloric acid. If pre-treatment was used carry out steps 8.1 to 8.7 inclusive; if pre-treatment was not used carry out steps 8.2 to 8.7 inclusive. Let the absorbances of the calibration standards be C_1 and C_2.	
	Calculation of results (note d).	
8.10	Calculate the concentration of antimony, A, from $A = \frac{S - B}{\bar{C} - B}$ μg/l Sb where $\bar{C} = \frac{C_1 + C_2}{2}$	(d) This calculation assumes a linear calibration curve and linearity must be checked. (See Section 9).

9 Checking the Linearity of the Calibration Curve

This procedure for checking the linearity of the calibration curve must be carried out on at least two independent occasions before the method is applied to any samples and regularly thereafter.

To a series of 2-litre conical flasks each containing 1.00 ± 0.01 litre of water and 3.0 ± 0.1 ml of 6M Hydrochloric acid add by pipette 0.00, 2.00, 4.00, 6.00, 8.00, 10.00 and 20.00 ml (all ± 0.02 ml) of standard antimony solution C respectively. These solutions contain 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 μg/l Sb respectively. Carry out the procedure described in steps 8.2 to 8.7 inclusive. Plot the absorbance against μg/l antimony for each solution. The calibration curve should be linear up to at least 2.0 μg/l Sb.

10 Change in Concentration Range of the Method

The procedure described can be used without modification to determine antimony in water and effluents at concentrations up to 2.0 μg/l. When the antimony concentration in the sample exceeds 2.0 μg/l it is necessary to take a smaller volume, Vml, of sample in step 8.1 or 8.2. It is then necessary to alter the calculation of the result (step 8.10) as follows:–

$$A = \frac{1000\ (S - B)}{V\ (\bar{C} - B)}$$

11 Sources of Error

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

11.1 Contamination

The techniques and working conditions should be critically examined to minimize any possibility of contamination.

11.2 Measurement of absorbance

The procedure used for measuring absorbance should be rigorously controlled to ensure satisfactory precision of measurement. The same cells should always be used for the reference and sample solutions, and 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 movement of the cell carrier should be kept scrupulously clean. Before every set of measurements the sample cell should be measured against the reference cell when both are filled with water. This will help indicate when the cells need cleaning and it will also enable the true absorbance of the blank to be determined.

11.3 Effect of antimony in the water used for the blanks

If antimony is present in the water used for the blank the results will be falsely low. Whether or not a correction is required for the effect depends on the magnitude of the error that can be tolerated and the concentration of antimony in the blank water. If it is suspected from a high blank value that the water is contaminated or a correction is required, the antimony in the blank water can be determined as follows:

Carry out steps 8.8 and 8.9 using 0.5 litre and 1.5 litre of water instead of 1 litre of water. Let the resulting absorbances be $B_0.5$ and $B_1.5$ respectively. The antimony concentration in the blank water A_B is given by:

$$A_B = \frac{B_{1\cdot5} - B_{0\cdot5}}{\bar{C} - Y} \quad \mu g/l$$

where $Y = \frac{B_{1\cdot5} + B_{0\cdot5}}{2}$

11.4 Interfering substances

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

12 Checking the Accuracy of Analytical Results

(see General Principles of Sampling and Accuracy of Results 1980, also published in the series).

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 test are possible and should be used as appropriate.[2]. As a minimum however, it is suggested that a standard solution of antimony of suitable concentration should be analysed at the same time and in exactly the same way as normal samples. (see Section 8). 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.

13 References

(1) Abu – Hilal AH and Riley JP, *Anal. Chim. Acta.* 1981, **131**, 175–186.
(2) Wilson AL and Cheeseman RV, Water Research Centre, *Technical Report* TR66, 1978.

Appendix

Estimation of the Accuracy of Analytical Results Using the Antimony Method

1 Introduction

Quantitative investigation of the accuracy achievable when the antimony method is used appears to be limited to work at the Department of Oceanography, University of Liverpool. Before firmly recommending the method for general use, it is desirable to know the accuracy achievable in other laboratories. It would, therefore, be of great value if any laboratory using or considering the use of this method could estimate the accuracy of its own analytical results and report the findings to the Secretary of the 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 antimony in the sample analysed and on the type of sample, eg worse precision may be obtained with samples than with standard solutions. For these reasons the basic design recommended is the analysis of one portion of each of the following solutions on each of n days, where n is at least 5 and preferably up to 10.

Solution No.	Description
1	Blank *
2	Another Blank*
3	Standard solution containing 0.2 μg/lSb
4	Standard solution containing 2.0 μg/lSb
5	Typical sample.
6	Same sample spiked with 1.0 μg/lSb.

* 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 A8 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 those four solutions. For solutions 5 and 6 a total of at least 10 litres of typical sample are required. Prepare solution 6 each day when required by spiking solution 5 as follows; add with a pipette 10.0 ml of standard antimony solution C (see Section 5.13.3) to 1 litre of solution 5. When analysing solution 6 it may be necessary to take into account Section 11 and to take an appropriately smaller aliquot. The total period of the test may be any convenient time so long as the antimony 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 antimony from 100% may give an indication of the presence of interfering substances.

3 Evaluation of Results

The raw experimental results should be sent directly 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 calculation 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 responses 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 results 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 of zero concentration from:

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

where X_{1i} = the result for solution 1 for 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 antimony in solution 6 from:

$$R = (1.01\ \bar{X}_6 - \bar{X}_5) \times 100.$$

Where $\bar{X}_5$ = the mean value of the results for solution 5.
Where $\bar{X}_6$ = the mean value of the results for solution 6.

3.6 Summarize the results as in the following table:

Solution	No of results	Mean antimony concentration µg/l	Standard deviation µg/l	Mean Recovery %
1 and 2 Blanks	2n =			–
3 Standard 0.2 µg/l Sb	n =			–
4 Standard 2.0 µg/l Sb	n =			–
5 Sample . . .	n =			–
6 Solution 5 + 1.0 µg/l Sb	n =			

†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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