Chromium in Raw and Potable Waters and Sewage Effluents 1980

Methods for the Examination of Waters and Associated Materials

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Two methods, both tentative

Methods for Examination of Waters and Associated Materials.

Two methods for the determination of chromium in waters are described in this booklet.

The first, method A, is based on concentration of the sample by evaporation followed by atomic absorption spectrophotometry and is suitable for raw and potable waters and sewage effluents.

The second, method B, is based on the spectrophotometric measurement of the coloured chromium diphenylcarbazide complex and is suitable for raw and potable waters.

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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; and 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards.

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 a 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 one 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 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 comittees 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 non-metallic substances
6.0 Organic impurities
7.0 Biological methods
8.0 Sludge and other solid analysis
9.0 Radiochemical methods

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

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

TA DICK
Chairman

LR PITTWELL
Secretary

4 December 1980

Method A

Chromium in Raw and Potable Waters and Sewage Effluents by Atomic Absorption Spectrophotometry Tentative Method (1980 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 chromium is expressed as the element (Cr).

A1.1	Substance determined	Forms of chromium likely to occur in waters and sewage effluents.
A1.2	Type of sample	Raw and potable waters, sewage effluents.
A1.3	Basis of method	Fivefold concentration by evaporation, incorporation of 2% m/V ammonium perchlorate in final solution in order to minimize interference effects, followed by atomic absorption spectrophotometry in the air-acetylene flame.
A1.4	Range of application	Up to 400 μg/l
A1.5	Calibration curve	Linear to 400 μg/l

A1.6 Standard deviation†

	Added chromium concentration μg/l	Within batch standard deviation μg/l	Degrees of freedom
*	0(a)	0·88	9
	10(a)	0·93	9
	50(a)	2·10	8
**	0(a)	1·15	9
	200(a)	3·14	9
***	0(a)	1.95	7
	100(a)	2·91	7
	200(a)	4·00	7

	Added chromium concentration μg/l	Total standard deviation (c) μg/l	Degrees of freedom
**	0(a)	1·30	9
	20(b)	1·60	17
	200(b)	4·77	14
	400(b)	11·34	13

A1.7	Limit of detection†(a)(d)	3·2–7·4 μg/l (with 7–9 degrees of freedom).
A1.8	Sensitivity (a)	200 μg/l gives an absorbance of approximately 0·05.
A1.9	Bias	Not known.
A1.10	Interferences	See Section 3.

A1.11	Time required for analysis	The total sample preparation and analytical measurement times for a batch of 15 samples are 2 hours and 1 hour respectively.

† These data were obtained using a method similar to that given here, but which prescribed only one aspiration of the blank solution (see Section A9). The method given here should give improved precision (particularly at low determinand concentrations) and a lower limit of detection.

* These results were obtained at the Laboratory of the Government Chemist[1].

** These results were obtained at Severn-Trent Water Authority (Malvern Regional Laboratory)[1].

*** These results were obtained at Yorkshire Water Authority (Head Office Laboratory, Leeds)[1].

a. Deionized water spiked with the stated chromium concentration.

b. Tap water spiked with the stated chromium concentration. (The natural chromium level in the tap water was below the detection limit.)

c. Duplicate analyses on each of nine days.

d. Range for the three participating laboratories.

A2 Principle

The method is based upon the atomic absorption spectrophotometric measurement of the chromium content of the acidified analyte solution after a fivefold concentration by evaporation. The measurement is carried out at 357·9 nm with background correction at 357·3 nm. In order to minimize interference effects the determination is carried out in a non-luminous air-acetylene flame and 2% m/V ammonium percholorate is incorporated into the final solution[2].

A3 Interferences

The effect of other substances on the determination of chromium is shown in Table 1.

Table 1. Effect of other substances on the method.

	Other substance	Other substance added as	Concentration of other substance (mg/l)	Effect in μg/l Cr of other substances at a chromium concentration of (μg/l) (e) 0·0	50·0	200·0
*	Calcium (as Ca^{2+})	chloride	500	3·3	3·0	
	Magnesium (as Mg^{2+})	chloride	100	1·7	2·0	
	Calcium (as Ca^{2+})	chloride	500			
	Magnesium (as Mg^{2+})	chloride	100	6·1	5·0	
	Sodium (as Na^{+})	chloride	500			
	Potassium (as K^{+})	chloride	100			
	Sulphate (as SO_4^{2-})	sulphuric acid	1000	3·8	7·2	
	Sulphate (as SO_4^{2-})	sulphuric acid	100	1·6	2·8	
	Phosphate (as PO_4^{3-})	potassium dihydrogen	100	<1·5	1·3	
	Hexametaphosphate (as PO_4^{3-})	sodium	100	<1·5	−1·3	
	Cobalt (as Co^{2+})	chloride	5			
	Copper (as Cu^{2+})	chloride	5			
	Iron (as Fe^{3+})	chloride	5			
	Manganese (as Mn^{2+})	chloride	5	3·2	1·4	
	Nickel (as Ni^{2+})	chloride	5			
	Lead (as Pb^{2+})	chloride	5			
	Zinc (as Zn^{2+})	chloride	5			
**	Calcium (as Ca^{2+})	chloride	100			
	Magnesium (as Mg^{2+})	chloride	20	−2·0		−8·0
	Detergent	Manoxol OT	10			

* These results were obtained at the Laboratory of the Government Chemist[1].

** These results were obtained at Severn-Trent Water Authority (Malvern Regional Laboratory)[1].

Other substance	Other substance added as	Concentration of other substance (mg/l)	Effect in μg/l Cr of other substances at a chromium concentration of (μg/l) (e) 0·0	50·0	200·0
Calcium (as Ca^{2+})	chloride	100			
Magnesium (as Mg^{2+})	chloride	20			
Sulphate (as SO_4^{2-})	sodium	100		3·0	−1·0
Sodium (as Na^{+})	sulphate	48			
Calcium (as Ca^{2+})	chloride	400			
Magnesium (as Mg^{2+})	chloride	40			
Sulphate (as SO_4^{2-})	sodium	100		2·0	−5·0
Sodium (as Na^{+})	sulphate	48			
Calcium (as Ca^{2+})	chloride	100			
Magnesium (as Mg^{2+})	chloride	20			
Ammonium (as N)	nitrate	180		2·0	−1·0
Nitrate (as N)	ammonium	180			
Calcium (as Ca^{2+})	chloride	100			
Magnesium (as Mg^{2+})	chloride	20		−1·0	0·0
Silica (as SiO_2)	sodium silicate	20			
Calcium (as Ca^{2+})	chloride	200			
Magnesium (as Mg^{2+})	chloride	20			
Zinc (as Zn^{2+})	chloride	20		−2·0	−6·0
Manganese (as Mn^{2+})	chloride	20			
Calcium (as Ca^{2+})	chloride	100			
Magnesium (as Mg^{2+})	chloride	20		2·0	−2·0
Phosphate (as PO_4^{3-})	diammonium hydrogen	10			

(e) If the other substances did not interfere the effect would be expected (95% confidence) to lie within the ranges of 0·0±2·7μg/l and 0·0±5·6μg/l Cr at concentrations of 0·0 and 50·0μg/l Cr respectively for Laboratory * and 0·0±2·6μg/l and 0·0±6·6μg/l Cr at concentrations of 0·0 and 200·0μg/l Cr respectively for Laboratory**.

A4 Hazards

Ammonium perchlorate is a potentially hazardous chemical and any spillage of the solid or its solutions should be throughly rinsed away with copious quantities of water to avoid any subsequent fire risk. The instructions in the method must be rigidly adhered to and the technique must not be scaled up or the risk of explosion could become significant. A safety screen should be used during the evaporation stage (see Section A9). Although numerous tests using the enforced evaporation to dryness and samples containing vegetable oils, glucose and digested sewage sludges did not result in an explosive reaction[2], the method should not be used with samples containing large amounts of organic matter.

A5 Reagents

All reagents and standard solutions should be stored in polyethylene bottles unless otherwise stated. Analytical reagent grade chemicals are suitable unless otherwise stated.

A5.1 Water

The water used for blank determinations and for preparing reagents and standard solutions should have a chromium 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 should be suitable.

A5.2 3% V/V Hydrochloric acid (wash solution)

Dilute 30±1 ml of hydrochloric acid (d_{20}1.18) with water to 1 litre in a measuring cylinder.

A5.3 10% V/V Hydrochloric acid

Dilute 100±1 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder.

A5.4 25% V/V Hydrochloric acid

Dilute 250±2 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder.

A5.5 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.

A5.6 10% m/V Ammonium perchlorate solution

Dissolve 50.0±0.1 g of ammonium perchlorate in about 450 ml of water and dilute with water to 500 ml in a calibrated flask. Store in a borosilicate glass bottle with a polyethylene stopper. This solution is commercially available.

A5.7 6% m/m Hydrogen peroxide (20 volume)

A5.8 Standard chromium solutions

A5.8.1 Solution A: 1 ml contains 1 mg chromium

Dissolve 1.414±0.001 g of potassium dichromate, dried at 105°C for 1 hour, in about 450 ml of water containing 5 ml of hydrochloric acid (d_{20} 1.18). Dilute with water to 500 ml in a calibrated flask. This solution is stable for at least three months.

A5.8.2 Solution B: 1 ml contains 20 μg chromium

Dilute 10.00 ±0.05 ml of *solution A* with water to 500 ml in a calibrated flask containing 10.0±0.5 ml of hydrochloric acid (d_{20} 1.18). This solution is stable for at least two months.

A5.8.3 Solution C: 1 ml contains 1 μg chromium

Dilute 10.00±0.05 ml of *solution A* with water to 500 ml in a calibrated flask containing solution should be freshly prepared before use.

A5.9 Aluminium oxide antibumping granules

The granules should be boiled in 50% V/V hydrochloric acid for one hour, and then washed thoroughly with deionized water, dried at 105°C and stored in a clean polyethylene or glass container.

A6 Apparatus

A6.1 An atomic absorption spectrophotometer equipped for an air-acetylene flame and with a chromium hollow-cathode lamp. A corrosion resistant (non-stainless steel) nebulizer and a titanium burner **must** be used. A lead hollow-cathode lamp is required for the sequential background correction (step A9.16). A general guide to the use of atomic absorption is given in Reference 3.

A6.2 100-ml borosilicate tall form beakers with spout. These beakers should be engraved at approximately the 5 ml. level.

A6.3 10-ml graduated borosilicate (0.1 ml divisions) tubes with ground glass stoppers.

A6.4 Cleanliness

Cleanliness is essential for this determination. If possible, apparatus should be reserved solely for chromium determinations. Clean all new glass and polyethylene ware by soaking in 10% V/V hydrochloric acid for 2 days. Rinse thoroughly with water. Thereafter a thorough rinse in 10% V/V hydrochloric acid followed by rinsing with water after each batch of derterminations should suffice. The 10-ml graduated tubes should regularly be cleaned using hot laboratory detergent solution and THOROUGHLY rinsed out with deionized water. Do not use glassware which has been cleaned in chromic acid.

A7 Sample Collection and Preservation

Clean a polyethylene bottle by the procedure described in Section A6.4, add 2.00 ±0.05 ml of 50% V/V hydrochloric acid per litre of sample to be collected and then collect the sample.

A8 Sample Pretreatment

The method involves prolonged simmering of the sample aliquot with hydrochloric acid at a final acid concentration of about 20% V/V hydrochloric acid and this should solubilize any chromium in natural and waste water samples.

A9 Analytical Procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE. A SAFETY SCREEN SHOULD BE USED DURING THE SIMMERING STEPS A9.2 AND A9.3.

Step	Experimental Procedure	Notes
	Analysis of samples	
A9.1	Add 50.0 ±0.5g of the sample into a 100-ml graduated borosilicate beaker, add 4.00 ±0.1 ml of 25% V/V hydrochloric acid, 2.00±0.05 ml of 10% m/V ammonium percholate solution and 4 or 5 acid washed aluminium oxide anti-bumping granules.	
A9.2	Place the beakers on a hot plate (mounted in a fume cupboard) and set the temperature control so that GENTLE simmering occurs. When the solution volume decreases to 20 ±5 ml add 0.50±0.05 ml of 6% m/m hydrogen peroxide (note a).	(a) This ensures than any Cr (VI) is reduced to Cr (III). The interference effects were assessed using Cr (III).
A9.3	Continue simmering until the final volume is 5±1 ml, and allow to cool.	
A9.4	Transfer the solution to a 10-ml graduated borosilicate tube and carefully wash out the beaker using three 1.0 ml washes of water (note b). Dilute with water to 10 ml, stopper the tube and shake to mix the contents.	(b) A 200µl plastic pipette tip fitted to a wash bottle is useful for this operation.
A9.5	Proceed to the atomic absorption stage, step A9.11.	
	Blank determination	
A9.6	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 100-ml graduated borosilicate beaker add 50.0±0.5 ml of water, 4.0±0.1 ml of 25% V/V hydrochloric acid, 2.00±0.05 ml of 10% m/V ammonium perchlorate and 4 or 5 acid washed anti-bumping granules.	
A9.7	Carry out steps A9.2 to A9.5.	
	Calibration Standards	
A9.8	Duplicate calibration standards must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for samples. (See Section A10). To each of two 100-ml borosilicate beakers add from a pipette 20.0 ml of standard chromium *solution C* and dilute with water to approximately 50 ml. This coprresponds to a chromium concentration of 400µg/litre (note c).	(c) For potable water analysis a solution corresponding to 100µg/litre chromium prepared by adding 5.0 ml of standard chromium *solution C* is more appropriate.
A9.9	Add 4.0±0.1 ml of 25% V/V hydrochloric acid, 2.00±0.05 ml of 10% m/V ammonium perchlorate and 4 or 5 acid washed aluminium oxide anti-bumping granules.	
A9.10	Carry out steps A9.2 to A9.5.	

Step	Experimental Procedure	Notes
	Atomic Absorption Stage	
A9.11	Set up the instrument according to the manufacturer's instructions. It is essential that a corrosion resistant (non-stainless steel nebulizer) and a titanium burner are used (note d). Set the wavelength to 357.9 nm. The acetylene flow should be adjusted so that the flame is on the verge of luminosity. (No yellow luminosity visible). Under these flame conditions interference effects are minimized.	(d) Stainless steel contains chromium and is rapidly corroded by chlorides. Satisfactory results have been observed using a stainless steel nebulizer when the hydrochloric acid used in the method was replaced by an equivalent amount of nitric acid (ie the final evaporated solutions should contain 10% V/V nitric acid (d_{20} 1.42)). However, performance characteristics have not been fully assessed using nitric acid.
A9.12	Aspirate the wash solution containing 3% V/V hydrochloric acid and adjust the instrument to read zero. Aspirate one of the calibration standards and adjust the instrument to give a suitable response (note e).	(e) With many modern atomic absorption instruments it is possible to use a direct concentration readout mode.
A9.13	Aspirate the wash solution and readjust the zero if necessary. Re-aspirate both the calibration standards with an aspiration of the wash solution after each. Let the response of the calibration standards be C_1 and C_2.	
A9.14	Aspirate the blank and then the wash solution and measure response of the blank B_1. Aspirate the samples with an aspiration of wash solution after each. Measure the instrument response of each sample S.	
A9.15	To check for any instrumental drift aspirate both calibration standards and the blank with an aspiration of wash solution after each and measure the instrument responses 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 $\bar{B}$.	
A9.16	Sequential background correction using the lead 357.3 nm non-resonance line should now be made to all samples. Aspirate each sample again with an aspiration of wash solution after each, using identical instrumental conditions with the lead lamp on the optical axis and the wavelength set to 357.3 nm. Measure the instrument response of each sample S_B (notes f and g).	(f) Automatic background correction can be used, but on many istruments this will result in a severely increased baseline noise level. (g) For samples with a conductivity below 400 μS/cm the background signal should be negligible.
	Calculation of results	
A9.17	Calculate the concentration A of chromium in the sample from	

$$A = \frac{S - S_B - \bar{B}}{\bar{C} - \bar{B}} \times 400 \ \mu g/l$$

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

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

S_B = Background correction response observed at 357.3 nm.

S = Sample response at 357.9 nm.

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 a series of 100-ml borosilicate beakers add, using a pipette, 2.50, 5.00, 10.00, 15.00 and 20.00 ml (all±0.02 ml) of standard chromium *solution C*. Dilute with water to a final volume of 50 ml. These solutions correspond to chromium concentrations of 50, 100, 200, 300 and 400 μg/litre respectively.

To each beaker add 4.0±0.1 ml of 25% V/V hydrochloric acid, 2.00±0.05 ml of 10% m/V ammonium perchlorate and 4 to 5 acid washed aluminium oxide anti-bumping granules. Carry out steps A9.2 to A9.5 inclusive. Plot the response against μg/l chromium.

The calibration curve is normally linear to 400 μg/l chromium; 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 A9.8 is not appropriate, nor is the range given in Section A1.4. In such a case the calibration standard chosen for step A9.8 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 chromium concentration in the sample is likely to exceed 400 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 50 ml of sample. Dilute with water to 50 ml and proceed as in step A9.1 onwards. It is necessary to alter the calculation of the result, step A9.17, as follows:

$$A = \frac{S - S_B - \overline{B}}{\overline{C} - \overline{B}} \times 400 \times \frac{50}{V} \quad \mu g/l \text{ chromium}$$

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 Contamination

It is desirable to carry out the analysis in a laboratory in which no appreciable amounts of chromium or its compounds are handled. The technique and working conditions should be critically examined and any source of contamination eliminated or minimized. In particular, it is desirable to reserve the glass apparatus used for the chromium 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 Chromium content of the water used for blank determinations

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

(a) To each of two 100.ml borosilicate glass beakers add 50.0 ±0.5 ml of water and 0.10±0.02 ml of 50% V/V hydrochloric acid.

(b) To each of two 250-ml borosilicate glass beakers add 100±1 ml of water and 0.10±0.02 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 50 ml. Add a further 50.0±0.5 ml of water to each beaker from (b) and continue heating until the volumes are reduced to 50±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 instrument responses be W_1^1 and W_2^1 for the two unheated beakers and W_1^{11} and W_2^{11} for the two heated beakers.

(e) The chromium content of the blank water is equivalent to an instrument response of

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

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

$$A_w = \frac{W}{\bar{C} - \bar{B}} \times 400\mu g/l \text{ chromium}$$

(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 chromium 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 A9.8 onwards give the necessary procedure. This procedure assumes a linear calibration curve and the linearity must be checked (see Section 10).

A13 Checking the Accuracy of Analytical Results

(For further information see Principles of Sampling and Accuracy of Results 1980, also published in this series.)

Once the methods have been put into normal 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 they should be used as appropriate. As a minimum, however, it is suggested that a standard solution of chromium of suitable concentration be analysed at the same time and in exactly the same way as normal samples. 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/646/50, paper SCA/4.2/21, July 1979.

(2) Thompson and Wagstaff K, Determination of Chromium in Natural Waters and Sewage Effluents by Atomic-Absorption Spectrophotometry using an Air-Acetylene Flame. Analyst 1979, **104**, 224.

(3) Thompson KC, Atomic Absorption Spectrophotometry. An Essay Review. Department of the Environment, 1979, HMSO, London.

Method B Chromium in Raw and Potable Waters by Spectrophotometry Tentative Method (1980) 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 Analytical Results 1980, also published in this series).

Note: Throughout this method chromium is expressed as the element (Cr).

B1.1	Substance determined	Forms of chromium capable of oxidation to Cr VI by potassium permanganate.
B1.2	Type of sample	Raw and potable waters.
B1.3	Basis of the method	Cr (III) is oxidised to Cr (VI) by permanganate. Cr (VI) is extracted into trioctylamine/chloroform and then reacted with diphenylcarbazide to form a violet coloured complex which is determined spectrophotometrically at 540 nm.
B1.4	Range of the method	Up to 100 μg/l
B1.5	Calibration curve	Linear to at least 100 μg/l
B1.6	Standard deviation (a) (within batch)	Chromium concentration (μg/l) / Standard deviation (μg/l): 10 (b) / 1·8; 50 (b) / 4·1; 100 (b) / 4·9. Each estimate with 4 degrees of freedom.
B1.7	Limit of detection (a)	5 μg/l (with 4 degrees of freedom).
B1.8	Sensitivity (a)	100 μg/l Cr gives an absorbance of approximately 0·22.
B1.9	Bias	None known.
B1.10	Interferences (a)	See Section 3.
B1.11	Time required for analysis (a)	Total analytical and operator times are the same and are typically 2 hours for a batch of six samples.

(a) These data were obtained at the Laboratory of the Government Chemist[1] using a spectrophotometer with 20-mm cells at 540 nm.

(b) Distilled water spiked with the stated chromium concentration.

B2 Principle

B2.1 The method is based upon the spectrophotometric measurement at 540 nm of the violet coloured complex formed by the reaction between chromium (VI) and diphenyl carbazide. Chromium (III) is converted to chromium (VI) by oxidation with potassium permanganate.

B2.2 It is necessary to separate the chromium from any iron present as it may cause interference. This is achieved by selectively extracting chromium (VI) into 5% m/V trioctylamine in chloroform prior to reacting with diphenyl carbazide[2,3]

B3 Interferences

The effect of other substances on the determination of chromium has been measured by the Laboratory of the Government Chemist[1] and is shown by Table 1.

Table 1. Effect of other substances on the method.

Other substance	Other substance added as	Concentration of other substance (mg/l)	Effect* in μg/l Cr of other substance at a chromium concentration of (0·0μg/l)	(50·0μg/l)
Calcium as Ca^{2+}	sulphate	500	+9·0	+7·1
Sodium as Na^{+}	sulphate	250	+6·2	+9·0
Chloride as Cl^{-}	sodium	250	+5·2	+6·2
Hexametaphosphate as PO_4^{3-}	sodium	50	−7·1	−3·8
Mercrury as Hg^{2+}	chloride	1	+2·9	+3·8
Iron as Fe^{3+}	sulphate	1	+2·9	+6·2
Iron as Fe^{3+}	sulphate	5	+9·0	+8·1
Manganese as Mn^{2+}	chloride	5	+4·3	+5·2
Copper as Cu^{2+}	chloride	5		
Nickel as Ni^{2+}	chloride	5	+11·0	+6·2
Cobalt as Co^{2+}	chloride	5		

* If the other substances did not interfere the effect would be expected to lie (95% confidence) between 0±4.2μg/l at 0μg/l chromium and 0±16.1μg/l at 50μg/l chromium.

B4 Hazards

B4.1 The sodium azide reagent (see Section B5.7) is toxic and should be regarded as a special hazard since it can liberate poisonous vapours on contact with water and acids. The solution should be prepared in a fume cupboard. Disposal of solutions containing azides to the laboratory drainage system can cause a potential explosion hazard. The azide present in solutions should be decomposed by adding either nitrite or a soluble sulphide before disposal to the drain.

B4.2 Additional hazards are the use of diphenyl carbazide (see Section B5.10) and chloroform (see Section B5.8) which are toxic. Avoid inhalation, skin contact and ingestion.

B5 Reagents

Analytical grade reagents are suitable unless otherwise specified. All reagents and standard solutions should be stored in polyethylene bottles unless otherwise specified.

B5.1 Water

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

B5.2 Soak acid

Carefully add 100±5 ml of nitric acid (d_{20} 1.42) to 400±10 ml of water and then add 300±10 ml of hydrochloric acid (d_{20} 1.18). Stir thoroughly to mix.

B5.3 30% V/V Nitric acid

Dilute 150±1 ml of nitric acid (d_{20} 1.42) with water to 500 ml in a measuring cylinder.

B5.4 50% V/V/ Sulphuric acid

Add slowly and cautiously with constant stirring 100±1 ml of sulphuric acid (d_{20} 1.84) to 75±5 ml of water contained in a beaker immersed in cold water. When cool transfer to a measuring cylinder and dilute with water to 200 ml.

B5.4.1 1M Sulphuric acid (approximately)

Carefully add 55.0±0.5 ml of sulphuric acid (d_{20} 1.84) to approximately 800 ml of water. Cool and dilute with water to 1 litre in a measuring cylinder.

B5.4.2 0.2M Sulphuric acid (approximately)

Dilute 100±1 ml of 1M sulphuric acid with water to 500 ml in a measuring cylinder.

B5.5 2M Sodium hydroxide (approximately)

Dissolve 8.0±0.1 g of sodium hydroxide in water, cool and dilute with water to 100 ml in a measuring cylinder.

B5.6 4% m/V Potassium permanganate

Dissolve 4.00±0.05 g of potassium permanganate in water and dilute with water to 100 ml in a measuring cylinder.

B5.7 0.5% m/V Sodium azide

This reagent is hazardous – see Section 4. Dissolve 0.50±0.01 g of sodium azide in water and dilute with water to 100 ml in a measuring cylinder.

B5.8 5% m/V Trioctylamine in chloroform

This reagent is hazardous – see Section 4.
Weigh 5.00±0.05 g of trioctylamine into a 100-ml calibrated flask and add chloroform to the mark.

B5.9 Anhydrous sodium sulphate

B5.10 Diphenylcarbazide (solid)

It has been found preferable to use solid diphenylcarbazide (DPC) rather than a solution of DPC because the stability of solutions of DPC was found to vary unpredictably with consequent changes in sensitivity. Even the solid has been known to show unusual variations in quality between batches and therefore a new calibration curve must be prepared for each new batch of DPC used. Distinct variations in sensitivity between batches are to be expected.

B5.11 Standard chromium solutions

B5.11.1 Solution A: 1 ml contains 500μg Cr

Dissolve 2.401 ±0.001 g of Chromium (III) potassium sulphate (chrome alum, $KCr(SO_4)_2.12H_2O$) in water, add 1.0 ±0.1 ml of 30% V/V nitric acid and dilute with water to 500 ml in a calibrated flask. This solution is stable for 3 months.

B5.11.2 Solution B: 1 ml contains 10μg Cr

Pipette 10.00±0.02 ml of standard chromium *solution A* into a 500-ml calibrated flask, add 0.20±0.02 ml of 30% V/V nitric acid and dilute with water to the mark. This solution should be freshly prepared when required.

B5.11.3 Solution C: 1 ml contains 0.5μg Cr

Pipette 5.00±0.02 ml of standard chromium *solution B* into a 100-ml calibrated flask, add 0.20±0.02 ml of 30% V/V nitric acid and dilute with water to the mark. This solution should be freshly prepared when required.

B6 Apparatus

B6.1 Glass ware and polyethylene ware

Cleanliness of glassware is absolutely essential for this determination. If possible, apparatus should be reserved solely for chromium determinations. Clean all glassware by filling or soaking in the soak acid for at least two hours and then rinse thoroughly with water before use. After use remove the taps from the separators and clean the taps, separators and other glassware by the procedure above. Do not use glassware which has been cleaned in chromic acid.

B6.2 A 200-ml separating funnel and a 100-ml separating funnel is required for each blank, sample and standard being determined.

B6.3 A spectrophotometer of prism or grating type or using a narrow band pass optical filter having its maximum transmission at 540 nm and 20-mm cells.

B7 Sample, Collection and Preservation

Clean a polyethylene bottle by the procedure given in Section B6.1, add to the empty bottle 2.0±0.1 ml of 30% V/V nitric acid per litre of sample to be collected and collect the sample. The acidification stabilizes chromium, minimizes the absorption on the walls of the bottle and assists in the dissolution of colloidal and particulate forms of chromium.

B8 Analytical Procedure

READ SECTION 4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Analysis of samples	
B8.1	Pipette 50.0±0.1 ml of sample (note a) into a 150-ml beaker. Add 2.0±0.1 ml of 50% V/V sulphuric acid and 4 drops of 4% m/V potassium permanganate. Heat to boiling and boil gently for 2 minutes.	(a) See Section 11; suitable for samples containing up to 100μg/l Cr. It may be possible to determine Cr (VI) only in samples by taking 50.0±0.1 ml of sample and starting at step B8.3. However, the applicability of this has not been checked.
B8.2	Add 1.00±0.05 ml of 0.5% m/V sodium azide solution, boil for a further 90±10 seconds and then cool to room temperature (note b).	(b) An ice bath may be used for speed if necessary.
B8.3	Add 50±1 ml of water and adjust the pH value of the solution to 1.8±0.1 with 1M sulphuric acid or 2M sodium hydroxide as appropriate. Transfer to a 200-ml separating funnel, rinse the beaker with 10±1 ml of water and add the rinsings to the separating funnel.	
B8.4	Add 10.0±0.1 ml of the 5% m/V trioctylamine/chloroform solution and 1.0 ±0.1 of anhydrous sodium sulphate. Shake well for 2 minutes±15 seconds and allow approximately 5 minutes quiescent standing for the phases to separate.	
B8.5	Run off the lower phase (note c), containing the chromium, into a 100-ml separating funnel containing 10.0 ±0.1 ml of 0.2M sulphuric acid and 0.50 ±0.50 g of anhydrous sodium sulphate. Add 0.15±0.02 g of diphenylcarbazide. Stopper and shake for 1 minute ±5 seconds. Allow 20±1 minutes quiescent standing for the colour to develop in the chloroform layer.	(c) Phase separating paper may prove useful in cases where emulsions are formed.
B8.6	Meanwhile set up the spectrophotometer according to the manufacturer's instructions. The wavelength required is 540 nm and water is used in the reference cell.	
B8.7	Run off the lower chloroform layer through a 10μm pore size filter paper (note d) into a 20-mm cell (note e). Measure the absorbance of the solution, S, within 15 minutes of completing step B8.5 (note f).	(d) Alternatively a cotton wool plug may be inserted in the stem of the separator. (e) Other sizes of cells may be used but the performance, characteristics quoted in Section B1 would no longer apply. (f) This reading should be taken within 35 minutes of adding the DPC in step B8.5.
	Blank determination	
B8.8	A blank must be run with each batch of determinations using the same reagents as for samples. Use 50.0±0.5 ml of water containing 0.10±0.01 ml of 30% V/V nitric acid instead of the sample and carry out steps 8.1 and 8.7 inclusive. Let the absorbance of the blank be B.	

Step	Experimental Procedures	Notes
	Determination of chromium in the water used for the blank (note g).	(g) This determination is not necessary if the chromium content of the water used for the blank is known or is negligible (see Section B12.2).
B8.9	Add 100±1 ml of water and 0.10±0.01 ml of 30% V/V nitric acid to a 150-ml beaker, cover the beaker with a watch glass raised slightly by means of a glass rod and evaporate until the volume is reduced to 50±5 ml. Repeat steps 8.1 to 8.7 inclusive. Let the absorbance be Y.	
B8.10	The absorbance W, due to chromium in 50 ml of water is given by $W = Y - B$ Determine the chromium concentration C_w (μg/l) in the water from W and the calibration curve.	
	Calculation of Results	
B8.11	Calculate the apparent absorbance, X, due to chromium in the sample from $X = S - B$ Determine the apparent chromium concentration Q_a in the sample from X and the calibration graph. Calculate the chromium concentration Q_r in the sample from $Q_r = Q_a + C_w \mu g/l$	

B9 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.

B10 Preparation of Calibration Curve

B10.1 To a series of 150-ml beakers add, using a pipette 0.00, 2.00, 4.00, 6.00, 8.00 and 10.00 (all±0.02 ml) of standard chromium *solution C*. Add to each beaker 0.10±0.01 ml of 30% V/V nitric acid and dilute with water to 50±2 ml. (Alternatively dilute with 50±2 ml of water containing 2.0±0.1 of 30% V/V nitric acid per litre). Carry out steps B8.1 to B8.7 inclusive. Subtract the absorbance of the blank from the absorbances of the other solutions and the plot the corrected results against the concentration of chromium. The above solutions are equivalent to 0, 20, 40, 60, 80 and 100 μg/l chromium respectively.

B10.2 The calibration curve has been found to be linear to at least 100 μg/l. The calibration curve should be checked at frequent intervals and must be checked whenever a new batch of diphenylcarbazide is used.

B11 Change in concentration range of the method

For samples containing chromium concentrations greater than 100 μg/l an appropriately smaller volume of sample should be taken. Dilute this volume V ml to 50 ml with water and add sufficient 30% V/V nitric acid so that there is the same total volume of 30% V/V nitric acid present as there would be in 50 ml of sample. The chromium concentration in the original sample is given by

$$Q_r = \frac{50}{V} \quad (Q_a + C_w) \ \mu g/l$$

B12 Sources of Error

The attention which 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.

B12.1 Contamination

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

B12.2 Effect of chromium in the water used for blank determinations

If the water used for the blank determination contains chromium 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 chromium in the blank water. The procedure in steps B8.9 and B8.10 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 analysis for which the same water is used for the blank.

B12.3 Interfering substances

See Section A3. The effect of possible interfering substances may be determined by analysing samples spiked with chromium 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 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 chromium of suitable concentration be analysed at 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.

B14 References

(1) Department of the Environment, File WS/646/50, paper SCA/4.2/20.

(2) Adam J and Pribil R, Talanta 18, 91, 1971.

(3) Adam J and Pribil R, Talanta 21, 616, 1974.

Appendix

Estimation of the Accuracy of Analytical Results using the Chromium Methods

1 Introduction

Quantitative investigation of the accuracy achievable when the chromium methods are used appears to be limited to work at the Severn-Trent and Yorkshire Water Authorities and the Laboratory of the Government Chemist for method A and the Laboratory of the Government Chemist for method B. Before firmly recommending the methods for general use, it is desirable to know the accuracy achievable in other laboratories. It would, therefore, be of great value if any laboratory using or considering the use of these methods, could estimate the accuracy of its own analytical results and report the findings to the Secretary of the Metals and Metalloids Working Group of the DOE/NWC Standing Committee of Analysts.*

The precision achieved and the effects of any interfering substances that may be present in samples are of particular interest. Any information on these aspects would be useful, but the value of such information would be greatly enhanced if it were obtained to a common plan so that the information can be compared and valid conclusions drawn. Accordingly, suggestions for a suitable experimental design and analysis of results are given in the following sections and it is strongly urged that laboratories follow this design whenever possible. The design has been chosen to be as simple as possible; more complex designs are possible and would give more information.

2 Basis of Suggested Tests

The limit of detection is governed by the within-batch variability of results at zero determinand concentration. The precision of analytical results may depend on the concentration of chromium 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	Method B
1	Blank†		
2	Another blank†		
3	Standard solution	10μg/l Cr	10μg/l Cr
4	Standard solution	200μg/l Cr	100μg/l Cr
5	Typical sample		
6	Same sample spiked with	200μg/l Cr	100μg/l Cr

†To be 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 B8 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 aspirated 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 (method A) or nitric acid (method B) 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 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 chromium solution B, as appropriate, to 100 ml of solution 5. When analysing solution 6 it may be necessary to take into account Section A11 or B11 and take an appropriately smaller aliquot. The total period of the tests may be any convenient time so long as the chromium

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 chromium 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 chromium in solution 6 from:

$$R = \frac{(1.01\ \bar{x}_6 - \bar{x}_5)}{200} \times 100 \qquad \text{for method A, or}$$

$$\frac{(1.01\ \bar{x}_6 - \bar{x}_5)}{100} \times 100 \qquad \text{for method B}$$

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 chromium concentration µg/l	Standard deviation µg/l	Mean recovery %
For method A:				
1 and 2 Blanks	2n=			—
3 Standard, 10µg/l Cr	n=			—
4 Standard, 200µg/l Cr	n=			—
5 Sample	n=			—
6 Solution 5+200µg/l Cr	n=			
For method B:				
1 and 2 Blanks	2n=			—
3 Standard, 10µg/l Cr	n=			—
4 Standard, 100µg/l Cr	n=			—
5 Sample	n=			—
6 Solution 5+100µg/l Cr	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
2 Marsham Street
LONDON SW1P 3EB
England

Address for Correspondence

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

The Secretary
The Standing Committee of Analysts
The Department of the Environment
2 Marsham Street
LONDON SW1P 3EB
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Mr WM Lewis	[1,2]	to Jan. 1980			
Mr PJ Long	[1]				

[1] Members of the Standing Committee

[2] Members of the Working Group

[3] Member of the Panel

* Occasional co-opted member (modifies preceding symbol)

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