Dissolved Potassium in Raw and Potable Waters Tentative Methods 1980

Methods for the Examination of Waters and Associated Materials

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Dissolved Potassium in Raw and Potable Waters Tentative Methods (1980 Version)

Methods for the Examination of Waters and Associated Materials

Two methods, both tentative, for the determination of potassium in raw and potable waters are described in order to cater for the availability of equipment in different laboratories. The first, method A, is based on flame photometry and the second, method B, is based on atomic absorption spectrophotometry.

A third instrumental method based on atomic emission spectrophotometry was investigated but this method was considered to be too sensitive for the determination of potassium in raw and potable waters and to offer no advantages over the atomic absorption spectrophotometric method.

Contents

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 manufacturer's 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 Biological 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 life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio-chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. If in doubt, it is safer to assume that the hazard may exist and take reasonable precautions, rather than to assume that no hazard exists until proved otherwise.

About this Series

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

The preparation of this series and its continuous revision is the responsiblity 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.

T A DICK
Chairman

L R PITTWELL
Secretary

4 December 1980

A. Dissolved Potassium in Raw and Potable Waters 1980 By Flame Photometry

Note: Throughout this method potassium is expressed as the element K.

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 dissolved potassium.
A1.2	Type of sample	Raw and potable waters.
A1.3	Basis of the method	Flame photometry.
A1.4	Range of application	Up to 10 mg/l without dilution. Higher levels may be determined after dilution to within this range.
A1.5	Calibration curve	Varies with the instrument; usually linear up to 10 mg/l but may show slight curvature.
A1.6	Standard deviation (total) (a)	Potassium concentration (mg/l) Standard deviation (mg/l) 3.00 (b) 0.038 5.00 (b) 0.072 8.00 (b) 0.065 1.61 (c) 0.028 4.61 (d) 0.061 (Each estimate has 19 degrees of freedom.)
A1.7	Limit of detection (a)	0.08 mg/l (with 10 degrees of freedom). The within batch standard deviation of a 0.5 mg/l potassium standard was 0.02 mg/l.
A1.8	Sensitivity (a)	1 mg/l K gives approximately 10% full scale deflection.
A1.9	Bias	Not known.
A1.10	Interference (a)	No important interferences known (see Section 3).
A1.11	Time required for analysis (a)	The total analytical and operator times are the same and for a batch of 10 samples are approximately 40 minutes.

(a) These data were obtained at the South West Water Authority[1].
(b) Distilled water spiked with the stated potassium concentration.
(c) Tap water.
(d) Tap water spiked to the stated potassium concentration.

A2 Principle

A2.1   Potassium is determined using a flame photometer of which several types are available. The sample, after dilution with water if necessary, is aspirated into a flame (usually a mixture of air and either town gas or propane or butane) of sufficient thermal energy to cause any potassium present to emit its characteristic radiation. The intensity of the emitted radiation is measured and related to the potassium concentration in the original sample.

A2.2   The method described measures potassium in the concentration range up to 10 mg/l. Many raw and potable waters will have potassium concentrations in this range and consequently the potassium concentration may be determined directly. However, some raw and potable waters will have potassium concentrations greater than 10 mg/l. Such waters should be diluted with potassium free water so that the potassium concentration is less than 10 mg/l prior to the determination. Waters containing suspended matter should be filtered through an acid (10% V/V hydrochloric acid) washed 0.45 μm filter prior to the determination. Potable waters do not normally require filtration.

A3 Interferences

A3.1   The effect of sulphate, chloride, calcium, sodium and lithium ions on the determination of 5 mg/l potassium has been determined by the South West Water Authority[2] and the results are reported in Table 1. Sulphate ions had a slight effect, and whilst this effect may be important in a few specific situations, generally it is not considered important in the determination of potassium in most raw and potable waters.

A3.2   The effect of the ionization buffer caesium on the determination of potassium in the range 0 to 10 mg/l has also been determined by the South West Water Authority[2]. This buffer had no effect over the potassium range tested and therefore its use is not recommended. Typical results at a potassium concentration of 5 mg/l given in Table 1.

Table 1

Substance	Concentration (mg/l)	Added as	Effect* in mg/l K at a potassium concentration of 5 mg/l
Sulphate as SO_4^{2-}	250	Ammonium sulphate	+ 0.30
Chloride as Cl^-	600	Ammonium chloride	+ 0.00
Calcium as Ca^{2+}	200	Calcium chloride	+ 0.20
Sodium as Na^+	100	Sodium chloride	+ 0.10
Lithium as Li^+	1,000	Lithium chloride	− 0.10
Caesium as Cs^+	1,000	Caesium chloride	+ 0.55

* If the substances did not interfere the effect would be expected (95% confidence) to lie with the range 0.00 ± 0.21 mg/l K.

A4 Hazards

The fumes from the flame photometer may contain toxic gases and therefore they should be ducted away to the outside atmosphere.

A5 Reagents

All reagents and standards for the determination of potassium must be stored in clean polyethylene bottles. Analytical reagent grade chemicals are essential unless otherwise stated.

A5.1 Water

The water used for blank determinations and for preparing reagents and standard solutions should have a potassium content which is negligible compared with the smallest concentration to be determined in the samples. Distilled water which has been passed through a mixed bed cation-anion exchanger is suitable.

A5.2 10% V/V Nitric acid

Dilute 100 ± 1 ml of nitric acid (d_{20} 1.42) with water to 1 litre.

A5.3 Standard potassium solutions

A5.3.1 *Solution A* 1 ml contains 1 mg potassium

Dissolve 1.907 ± 0.005 g of potassium chloride (dried for at least 1 hour at ($140\pm 10°C$) in water and dilute with water to 1 litre. This solution is stable for several months.

A5.3.2 *Solution B* 1 ml contains 100 μg potassium

Dilute 10.00 ± 0.02 ml of standard potassium *solution A* with water to 100 ml in a calibrated flask. This solution should be freshly prepared when required.

A6 Apparatus

A6.1 A flame photometer using an appropriate interference filter and equipped for an air/fuel flame. The fuel may be town gas, propane or butane.

A6.2 All glassware should be of borosilicate glass. All glass and polyethylene ware should be cleaned by filling with or soaking in 10% V/V nitric acid followed by thorough rinsing with water. If possible, the apparatus should be reserved for potassium determinations.

A6.3 Potassium is an ubiquitous element and precautions should be taken to guard the apparatus against contamination from, for example, dust, smoke, cleaning materials and perspiration.

A7 Sample Collection and Preservation

Collect the sample in a clean polyethylene bottle (see Section A6.2). Sample preservation is not required.

A8 Analytical Procedure

READ SECTION A4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Preparation of calibration curve (note a)	
A8.1	To a series of 100-ml calibrated flasks add 1.00, 2.50, 5.00, 7.50 and 10.00 ml (all ± 0.02 ml) of standard potassium *solution B* and dilute with water to the mark. These solutions contain 1.0, 2.5, 5.0, 7.5 and 10.0 mg/l K respectively.	(a) This calibration procedure must be carried out before analysis of each batch of samples.
A8.2	Set up the flame photometer according to the manufacturer's instructions for determining potassium. Aspirate water and adjust the scale reading to 0%. Aspirate the 10 mg/l K standard and adjust the scale reading to 100%. Repeat the aspiration of water and 10 mg/l potassium until the 0% and 100% readings respectively are obtained without the need for further adjustment. Aspirate water.	
A8.3	Aspirate the 1.0 mg/l K standard and measure the instrument response. Aspirate water. Aspirate the other calibration standards with an aspiration of water after each and measure the instrument response of each standard. Construct a calibration curve of potassium concentration against instrument response.	
	Filtration of samples	
A8.4	If the sample contains suspended matter a suitable portion should be filtered through an acid (10% V/V hydrochloric acid) washed 0.45 μm filter. If the sample does not contain suspended matter proceed to step A8.5.	
	Dilution of samples (note b)	
A8.5	If the sample or filtered sample contains or is likely to contain more than 10 mg/l potassium then an appropriate volume, V_1 ml, of the sample should be diluted with water to an appropriately larger volume, V_2 ml, so that the expected potassium concentration is less than 10 mg/l. The dilution factor $F = \dfrac{V_2}{V_1}$	(b) If the potassium concentration is expected to be less than 10 mg/l proceed directly to step A8.6.
	Analysis of samples	
A8.6	Aspirate the sample, filtered sample or diluted sample and measure the instrument response. Aspirate water. Aspirate the remaining samples with an aspiration of water after each and measure the instrument response (note c).	(c) Aspirate a 10 mg/l potassium standard after every 10 samples and readjust the instrument if necessary.
A8.7	When all samples and standards have been aspirated water should be aspirated for at least two minutes to cleanse the instrument.	

Calculation of the result

A8.8   If the sample was aspirated without dilution the potassium concentration is read directly from the calibration graph.

If the sample was diluted (step A8.5) determine the potassium concentration, A, in the diluted sample from the calibration graph and calculate the potassium concentration, B, in the original sample from

$$B = A \times F \text{ mg/l K}$$

A9   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.

A9.1   Contamination

See Section A6.3. The technique and working conditions should be critically examined and any important sources of contamination minimized.

A9.2   Interfering substances

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

A9.3   Calibration curve

The calibration curve for this method may be slightly non-linear in the specified range and the degree of non-linearity may vary from instrument to instrument. It is essential that a calibration curve be prepared (steps A8.1 to A8.3) before analysis of each batch of samples.

A10   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 potassium of suitable concentration be analysed at the same time and in exactly the same way as normal samples (see Section A8). 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.

A11   References

1. Department of the Environment, File WS/646/53, Papers SCA/4.3/32 and 35.
2. Department of the Environment, File WS/646/53, Papers SCA/4.3/33 and 35.

B. Dissolved Potassium in Raw and Potable Waters 1980 By Atomic Absorption Spectrophotometry

Note: Throughout this method potassium is expressed as the the element K.

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 soluble potassium.
B1.2	Type of sample	Raw and potable waters.
B1.3	Basis of the method	Atomic absorption spectrophotometry.
B1.4	Range of application (a)	Up to 10 mg/l
B1.5	Calibration curve (a)	Normally linear to 10 mg/l (see Section B9).

B1.6	Total standard deviation (a)	Potassium concentration (mg/l)	Total standard deviation (mg/l)
		0.00 (b)	0.034
		2.00 (b)	0.032
		8.00 (b)	0.119
		5.01 (c)	0.057
		7.00 (d)	0.129
		(Each estimation has 9 degrees of freedom.)	

B1.7	Limit of detection (a)	0.15 mg/l with 9 degrees of freedom.
B1.8	Sensitivity (a)	10 mg/l potassium gives an absorbence of approximately 0.75.
B1.9	Bias	None known.
B1.10	Interferences	None known, see Section B3.
B1.11	Time required for analysis (a)	The total analytical and operator times are the same and for a batch of 10 samples are approximately 30 minutes.

(a) These data were obtained at the Thames Water Authority[1] using this method and a single beam atomic absorption spectrophotometer with the burner rotated 20° to the optical axis.
(b) Distilled water spiked with the stated potassium concentration.
(c) Tap water.
(d) Tap water spiked with 2.00 mg/l potassium.

B2 Principle

B2.1   Potassium is determined by atomic absorption spectrophotometry by aspirating a sample (or an acified sample) containing 1,000 mg/l caesium as an ionization suppressant directly into an air/acetylene flame. The wavelength required is 769.9 nm. An important requirement is that the atomic absorption spectrophotometer must be fitted with a suitable red sensitive photomultiplier.

B2.2   The method described measures potassium in the concentration range up to 10 mg/l. Some waters will have potassium concentrations greater than 10 mg/l and such waters should be diluted with water so that the potassium concentration is less than 10 mg/l prior to the determination. Waters containing suspended matter should be filtered through an acid (10% V/V hydrochloric acid) washed 0.45 μm filter prior to the determination. Potable waters do not normally require filtration.

B3 Interferences

B3.1   Investigations carried out by Thames Water Authority have shown that 1,000 mg/l caesium is required as an ionization suppressant during the determination.

B3.2   The effect of various potential interfering substances has been determined by Thames Water Authority[2] and the results are given in Table 2.

Table 2

Other Substance	Concentration (mg/l)	Added as	Effect* in mg/l potassium at a potassium concentration of:	
			2.00 mg/l	8.00 mg/l
Sulphate as SO_4^{2-}	250	Ammonium sulphate	− 0.03	+ 0.05
Chloride as Cl^-	600	Ammonium	− 0.10	− 0.31
	600	sodium	− 0.09	− 0.35
	600	hydrogen	− 0.06	− 0.18
Sodium as Na^+	100	Sodium chloride	0.00	+ 0.04
Calcium as Ca^{2+}	200	Calcium nitrate	− 0.04	− 0.27

*   If the other substance did not interfere the effect would be expected (95% confidence) to lie between 0.00 ± 0.03 and 0.00 ± 0.07 at 2.00 mg/l K and 8.00 mg/l K respectively.

B4 Hazards

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

B5 Reagents

All reagents and standards for the determination of potassium must be stored in clean polyethylene bottles. Analytical reagent grade chemicals are essential unless otherwise stated.

B5.1 Water

The water used for blank determinations and for preparing reagent and standard solutions should have a potassium content which is negligible compared with the smallest concentration to be determined in samples. Distilled water which has been passed through a mixed bed cation/anion exchanger is suitable.

B5.2 Standard potassium solution 1 ml contains 0.2 mg potassium

Dissolve 0.381 ± 0.005 g of potassium chloride (dried for at least 1 hour at $140 \pm 10°C$) in water and dilute with water to 1 litre. This solution is stable for several months.

B5.3 Hydrochloric acid (d_{20} 1.18)

B5.3.1 *10% V/V Hydrochloric acid*

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

B5.4 10% V/V Nitric acid

Dilute 100 ± 1 ml of nitric acid (d_{20} 1.42) with water to 1 litre.

B5.5 10% m/V Caesium solution

Dissolve 127 ± 1 g of caesium chloride in water and dilute with water to 1000 ml in a calibrated flask.

B6 Apparatus

B6.1 An atomic absorption spectrophotometer equipped for an air/acetylene flame and with a potassium hollow cathode lamp, also fitted with a suitable red sensitive photomultiplier.

B6.2 All glassware should be of borosilicate glass. Both glass and polyethylene ware should be cleaned by filling with or soaking in 10% V/V nitric acid followed by thorough rinsing with water. If possible, the apparatus should be reserved for potassium determinations.

B6.3 Potassium is an ubiquitous element and precautions should be taken to guard the apparatus against contamination from, for example, dust, smoke, cleansing materials and perspiration.

B7 Sample Collection and Preservation

Collect the sample in a clean polyethylene bottle (see Section B6.2). Sample preservation by acidification is not necessary. However, the determination can be carried out on samples preserved by acidification (hydrochloric or nitric acid) provided that all samples, standards and blanks contain the same concentration of acid.

B8 Analytical Procedure

READ SECTION B4 ON HAZARDS BEFORE STARTING THIS PROCEDURE

Step	Experimental Procedure	Notes
	Filtration of samples	
B8.1	If the sample contains suspended matter a suitable portion should be filtered through an acid (10% V/V hydrochloric acid) washed 0.45 μm filter. If the sample does not contain suspended matter proceed to step B8.2.	
	Dilution of samples (note a)	
B8.2	If the sample or filtered sample contains or is likely to contain more than 10 mg/l potassium then an appropriate volume, V_1 ml, of the sample should be diluted with water to an appropriately larger volume, V_2 ml, so that the expected potassium concentration is less than 10 mg/l. The dilution factor $F = \dfrac{V_2}{V_1}$	(a) If the potassium concentration is expected to be less than 10 mg/l proceed directly to step B8.3
	Preparation of samples	
B8.3	Add 1.00 ± 0.02 ml of 10% m/V caesium solution to 100 ± 5 ml of sample, filtered sample or diluted sample in a measuring cylinder and mix well.	
	Blank determination (note b)	
B8.4	A blank must be run with each batch (eg up to 10 samples) of determinations using the same batch of reagents as for samples. Add 1.00 ± 0.02 ml of 10% m/V caesium solution to 100 ± 5 ml of water in a measuring cylinder and mix well.	(b) If the sample was preserved by acidification then the same concentration of acid must be added to the blank and calibration standards.
	Calibration standards (note b)	
B8.5	Duplicate calibration standards must be run with each batch (up to 10 determinations) using the same batch of reagents as for samples. Dilute 5.00 ± 0.01 ml of standard potassium solution (Section B5.2) with water to 100 ml in a calibrated flask (note c). Add 1.00 ± 0.02 ml of 10% m/V caesium solution and mix well. Prepare another identical standard.	(c) This calibration standard contains 10 mg/l potassium.
	Atomic absorption stage	
B8.6	Set up the instrument according to the manufacturer's instructions for an air/acetylene flame. The wavelength required is 769.9 nm.	
B8.7	Aspirate water and adjust the zero. Aspirate one of the calibration standards and adjust the instrument to give a suitable response.	
B8.8	Aspirate water and readjust the zero if necessary. Aspirate both the calibration standards with an aspiration of water after each and measure the instrument responses C_1 and C_2.	

Step	Experimental Procedure	Notes

B8.9 Aspirate the blank and measure the instrument response B_1. Aspirate water. Aspirate the samples (step B8.3) with an aspiration of water after each. Measure the instrument response of the sample S. (note d).

(d) If the sample contains more than 10 mg/l K see step B8.2.

B8.10 To check for any instrument drift aspirate both calibration standards and the blank with an aspiration of water 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 B_1 and B_2 are in satisfactory agreement calculate the means $\bar{C}$ and $\bar{B}$.

Calculation of Results (note e)

B8.11 Calculate the potassium concentration, A, in the sample from

$$A = \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 10 \text{ mg/l}$$

for an undiluted sample and from

$$A = F \times \frac{S - \bar{B}}{\bar{C} - \bar{B}} \times 10 \text{ mg/l}$$

for a diluted sample.

(e) This calibration assumes a linear calibration curve. Linearity must be checked (see Section B9).

B9 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.

Pipette into a series of 100-ml calibrated flasks 1.00, 2.00, 3.00, 4.00 and 5.00 ml (all ± 0.01 ml) of standard potassium solution (see Section B6.2) and dilute with water to 100 ml. These solutions contain 2, 4, 6, 8 and 10 mg/l potassium respectively. Add 1.00 ± 0.02 ml of 10% m/V caesium solution to each flask and mix well. Carry out the procedure given in steps B8.6 to B8.10 inclusive. Plot the instrument response against mg/l potassium.

The calibration curve is normally linear to 10 mg/l potassium; 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 B8.5 is not appropriate, nor is the range given in B1.4. In such a case the calibration standard chosen for step B8.5 should be the highest concentration on the linear portion of the curve and the concentration range of the method should be adjusted accordingly.

B10 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.

B10.1 Contamination

See Section B6.3. The technique and working conditions should be critically examined and any important sources of contamination minimized.

B10.2 Interfering substances

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

B10.3 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 duplicate calibration standard must be run for each batch of analyses and steps B8.5 onwards give the necessary procedure. This procedure assumes a linear calibration curve and linearity must be checked (see Section B9).

B11 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 potassium of suitable concentration be analysed at the same time and in exactly the same way as normal samples (see Section B8). 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.

B12 References

1. Department of the Environment, File WS/646/53, Paper SCA/4.3/38
2. Department of the Environment, File WS/646/53, Paper SCA/4.3/39.

Appendix

Estimation of the Accuracy of Analytical Results Using the Potassium Methods

1 Introduction	Quantitative investigation of the accuracy achievable when the potassium methods are used appears to be limited to work at South West Water Authority for Method A and the Thames Water Authority 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 potassium 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	1 mg/l K	1 mg/l K
4	Standard solution	5 mg/l K	6 mg/l K
5	Typical sample		
6	Same sample spiked with	5 mg/l K	6 mg/l K

[+] 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 A8 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 analyses. Solutions 1 to 4 should be prepared each day exactly as described in the method.

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 potassium solution A (see A5.3.1) to 200 ml of solution 5 for Method A and 3.0 ml of standard potassium solution (see B5.2) to 100 ml of solution 5 for Method B. When analysing solution 6 in Method B it may be necessary

to take into account step B8.2 note a and to take an appropriately smaller aliquot. The total period of the tests may be any convenient time so long as the potassium concentration in solution 5 does not change appreciably (up to 2 weeks). The results of the analyses of solution 5 and 6 will provide a check on the effect of sample type on precision. Any deviation of the recovery of spiked potassium 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:

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

where X_i = the result from the ith batch

$\overline{X}$ = 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 potassium in solution 6 from:

$$R = \frac{(1.005\,\overline{X}_6 - \overline{X}_5)}{5} \times 100 \quad \text{for method A, or}$$

$$R = \frac{(1.03\,\overline{X}_6 - \overline{X}_5)}{6} \times 100 \quad \text{for Method B}$$

where $\overline{X}_5$ = the mean value of the results for solution 5

$\overline{X}_6$ = the mean value of the results for solution 6.

3.6 Summarize the results as in the following table:

Solution	No of results	Mean Potassium Concentration mg/l	Standard Deviation %	Mean Recovery %
For Method A:				
1 and 2 Blanks	$2n =$			—
3 Standard, 1 mg/l K	$n =$			—
4 Standard, 5 mg/l K	$n =$			—
5 Sample	$n =$			—
6 Solution 5 + 5 mg/l K	$n =$			
For Method B:				
1 and 2 Blanks	$2n =$			—
3 Standard, 1 mg/l K	$n =$			—
4 standard, 6 mg/l K	$n =$			—
5 Sample	$n =$			—
6 Solution 5 $\times$ 6 mg/l K	$n =$			

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

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
2 Marsham Street
LONDON SW1P 3EB
England

Department of the Environment/National Water Council

Standing Committee of Analysts

Members of the Committee Responsible for this Method

Dr GI Barrow[1]
Dr GA Best[1]   from 1980
Mr W Carr[2,3]
Dr JM Carter[1]
Dr GW Clayfield[1]
Mr BEP Clement[1]
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Mr MG Firth[2]   to 1980
Dr J Gardiner[1,2*]   from 1980
Mr GI Goodfellow[1]   from 1980
Mr K Goodhead[1]   to 1980
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Mr OD Hydes[2,3*]
Mr RH Jenkins[2]
Mr WM Lewis[1,2,3]   to 1980
Mr PJ Long[1]

Mr GF Lowden[2*3]   to 1980
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Dr AM Ure[1]
Mr BT Whitham[1]
Mr AL Wilson[1]   to 1980

[1] Members of the Standing Committee
[2] Members of the Working Group
[3] Members of the Panel
* Occasional co-opted member (modifies the preceding symbol)