# Methods for the Examination of Waters and Associated Materials

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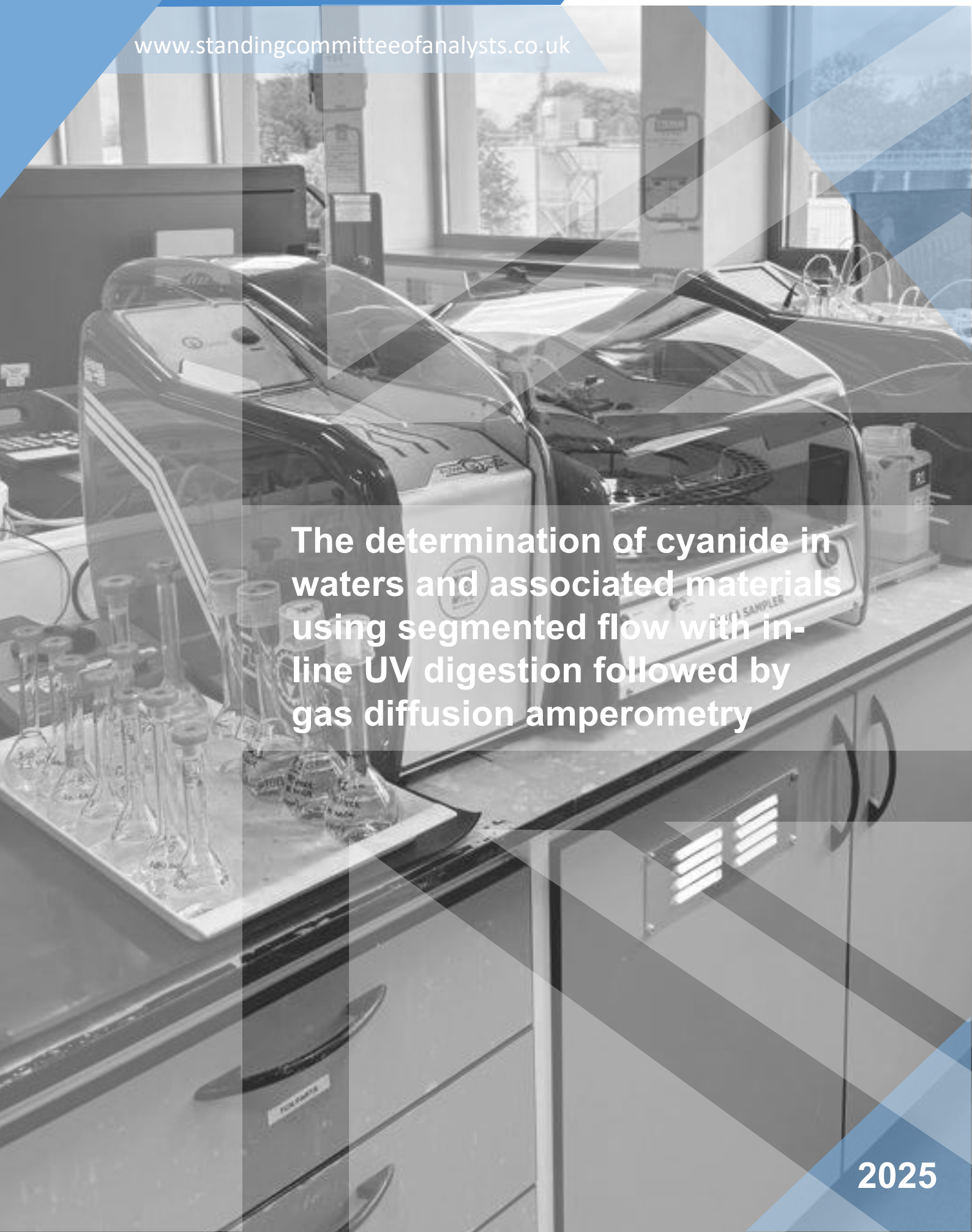

## The determination of cyanide in waters and associated materials using segmented flow with in-line UV digestion followed by gas diffusion amperometry

2025

**The determination of cyanide in waters and associate materials using segmented flow with in-line UV digestion followed by gas diffusion amperometry**

This booklet is an additional method of cyanide analysis, not presented in any Methods for the Examination of Waters and Associated Materials book before and complements The Determination of Cyanide in Waters and Associated Materials published in 2007. Only limited performance data is available for this newly published method.

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## Foreword

Whilst specific commercial products may be referred to in this document, this does not constitute an endorsement of these products but serves only as an illustrative example of the type of products available. Equivalent products are available and it should be understood that the performance of the method might differ when other materials are used, and all should be confirmed by validation of the method.

**Contents**

## About This Series

### Introduction

This booklet is part of a series intended to provide authoritative guidance on recommended methods of sampling and analysis for determining the quality of drinking water, ground water, river water and sea water, wastewater and effluents as well as sewage sludges and biota.

In addition, short reviews of the most important analytical techniques of interest to the water and sewage industries are included.

### Performance of methods

Ideally, all methods should be fully evaluated with results from performance tests. These methods should be capable of establishing, within specified or pre-determined and acceptable limits of deviation and detection, whether or not any sample contains concentrations of parameters above those of interest.

For a method to be considered fully evaluated, individual results from at least three laboratories should be reported. The specifications of performance generally relate to maximum tolerable values for total error (random and systematic errors) systematic error (bias) total standard deviation and limit of detection - often, full evaluation is not possible and only limited performance data may be available.

In addition, good laboratory practice and analytical quality control are essential if satisfactory results are to be achieved.

## Standing Committee of Analysts

The preparation of booklets within the series "Methods for the Examination of Waters and Associated Materials" and their continuing revision is the responsibility of the Standing Committee of Analysts (SCA) - Established 1972 by the Department of the Environment.

At present, there are several working groups, each responsible for one section or aspect of water quality analysis:

1. General principles of sampling and accuracy of results
2. Microbiological methods
3. Inorganic and physical methods, metals and metalloids
4. Organic methods
5. Biological, biodegradability and inhibition methods
6. Radiochemistry methods

The actual methods and reviews are produced by smaller panels of experts in the appropriate field, in co-operation with the working group and main committee. The names of those members principally associated with these methods are listed at the back of this booklet.

Publication of new or revised methods will appear on our website – the library for which serves as a record of the bona fide methods developed and produced by the Standing Committee of Analysts.

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Every effort is made to avoid errors appearing in the published text. If, however, any are found, please notify the Secretary.

secretary@standingcommitteeofanalysts.co.uk

Users should ensure they are aware of the most recent version they seek.

**Warning To Users**

The analytical procedures described in this booklet should only be carried out under the proper supervision of competent, trained analysts in properly equipped laboratories.

All possible safety precautions should be followed, and appropriate regulatory requirements complied with. This should include compliance with the Health and Safety at Work etc. Act 1974 and all regulations made under the Act, and the Control of Substances Hazardous to Health Regulations 2002 (SI 2002/2677). Where particular or exceptional hazards exist in carrying out the procedures described in this booklet, then specific attention is noted.

Numerous publications are available giving practical details on first aid and laboratory safety. Amongst such resources are:

HSE: Information about health and safety at work

RSC: Laboratory best practices

## 1 Introduction

This method is for the analysis of total cyanide which is defined as the sum of easily liberated and complex cyanides under the conditions used. It combines segmented flow injection analysis, with digestion by ultraviolet irradiation with subsequent gas diffusion of the formed cyanide gas, to be detected by amperometry.

## 2 Scope

The method determines cyanide ions, hydrogen cyanide and weak-acid dissociable complexes like those of lead, zinc, copper, manganese, and other stronger metal-cyanide complexes, like those of iron. It is applicable for raw, potable and waste waters.

Ultraviolet radiation is used to release cyanide from complex cyanides. Acidification converts the cyanide ion to hydrogen cyanide which passes through a gas only permeable membrane into a basic acceptor solution converting the hydrogen cyanide into the ion cyanide through ligand exchange and detected using a silver electrode. The range of application is up to 60 µg/l cyanide but can be extended by sample dilution. The limit of quantification is approximately 6.5 µg/l.

With an automated system, the signal from the first autosampler uptake takes approximately 20 min and subsequent uptakes require approximately 5 minutes per sample/standard. A new calibration is required for each new analytical run.

## 3 Principle

A set amount of sample is introduced into the analyser via a peristaltic pump. The flow is segmented by the controlled introduction of air into the sample channel. This flow is acidified before digestion which converts free cyanide ions to hydrogen cyanide (HCN) and aids the decomposition of some of the more easily dissociable compounds.

The UV digestion releases the cyanide ion from the complex cyanide species, and the resulting cyanide ion is also converted to hydrogen cyanide gas (HCN), by protonation.

The resulting HCN passes through a gas diffusion membrane and is captured into a basic acceptor solution. The HCN is converted back to cyanide ion, through a ligand exchange with the hydroxide ion and it is detected amperometrically using a silver electrode. The current generated is proportional to the amount of cyanide ion present.

## 4 Hazards

With only very few exceptions, cyanides are rapidly acting poisons following ingestion, inhalation, or absorption through the skin. Cyanide solutions should not be pipetted by mouth and fumes should not be inhaled. Skin contact should be avoided and any splashes involving contact with cyanide solutions should be washed off immediately. Immediate first aid facilities should be available if poisoning is suspected. Provision of qualified personnel to administer first aid should be considered in the event of cyanide poisoning.

Hydrogen cyanide is a toxic gas. Acidic solutions should not be mixed with cyanide containing solutions.

Citric acid and sodium hydroxide are corrosive substances and can cause chemical burns and serious skin and eye irritation. The solutions should be stored separately.

Bismuth (III) nitrate pentahydrate can cause skin, eye and respiratory irritation.

## 5 Interferences

Cyanide is incompletely recovered from certain complexes. Interferences may arise.

Oxidizing agents, like chlorine, decompose cyanides. Samples are treated with Sodium thiosulphate to remove it. Ascorbic acid as a dechlorinating agent is not recommended for chloraminated samples, due to the potential interference.[3]

It has been shown that sodium thiosulphate can have an adverse effect on the conversion of complex cyanide to free cyanide (by ultraviolet digestion and distillation). A sodium thiosulphate concentration of 500 mg/L caused an apparent 30 % loss of complex cyanide, whereas a sodium thiosulphate concentration of 5 mg/L (whilst sufficient to destroy any free chlorine present) caused no apparent effect.[3]

The main interference arises from sulphide. A concentration of sulphide at 1 mg/L depresses results by about 13 %, and sulphide at 20 mg/L causes about 100 % depression. Thiocyanate interferes in the determination of total cyanide using ultraviolet irradiation.

Sulphide interacts with the silver electrode. The thiosulphate used to dechlorinate the samples can decompose in the UV chamber to form some sulphide. A solution of bismuth (III) pentahydrate is added online before the gas diffusion membrane to eliminate sulphide interferences. All solutions, samples and standards must be matrix matched.

Thiocyanates can produce a positive interference though decomposition to cyanide in the UV digestion chamber. This is minimized by using a UV lamp that operates in the narrowband of 350 - 370 nm.

Samples with a high level of alkalinity can experience issues with recovery, laboratory testing may be required to determine the sample alkalinity limit of the method.

## 6 Sample Collection and Preservation

Samples may be collected in plastic (for example polyethylene). Potable water, or other samples containing residual disinfectant should be de-chlorinated using sodium thiosulphate, for example.

As soon as possible after sampling, sodium hydroxide solution should be added to all aqueous samples. The final concentration of alkali should be such that the final pH is approximately 12.

The sodium hydroxide used for this purpose should contain negligible amounts of cyanide and wherever possible, the same specification of material should be used for the preservation of samples and for the preparation of calibration solutions.

Preserved samples should be stored in the dark at a temperature between 1 - 5˚C, to avoid light-induced decomposition of cyanide. The sample should be analysed as soon as possible after collection.

## 7 Reagents

Shelf life and storage conditions to be confirmed or determined by individual laboratories.

7.1 2.5% w/w Sodium Thiosulphate Solution

Quantitatively transfer 1.25 ± 0.05 g of sodium thiosulphate pentahydrate to a 50 ml volumetric flask containing approximately 40 ml of deionised water. Make up to the mark with deionised water.

7.2 Digestion Reagent

Slowly, quantitatively transfer 12 ± 0.5 g of sodium hydroxide into a 1000 ml volumetric flask containing approximately 400 ml deionised water. Mix to dissolve and make up to approximately 800 ml with deionised water. Quantitatively transfer 50 ± 0.1 g of citric acid. Allow to dissolve and make up to the 1000 ml mark with deionised water. Check the pH. It needs to be 3.83. If it is not, adjust accordingly with NaOH 1M or a citric acid solution 20%. Transfer to the relevant instrument container. Store at room temperature for up to 3 months.

7.3 0.1M Sodium Hydroxide Reagent

Quantitatively transfer 2 ± 0.1 g of sodium hydroxide into a 500 ml volumetric flask containing approximately 300 ml deionised water. Mix to dissolve and make up to the mark with deionised water. Transfer to the relevant instrument container. Store at room temperature for up to 1 month.

7.4 Bismuth (III) Pentahydrate Reagent, 1 g/L

Add a small amount of deionised water to a 1000 ml volumetric flask. Quantitatively transfer 1 ± 0.001 g of bismuth (III) nitrate pentahydrate into the flask and allow to dissolve. Add approximately 800 ml of deionised water. In the fume cupboard place the volumetric into a large container with cold water. Using a 100 ml measuring cylinder or dispenser slowly add 55 ml of concentrated sulphuric acid to the flask, using appropriate laboratory safety procedures for use of sulphuric acid. Let it cool down completely (it is advisable to let it stand overnight) and make up to the mark with deionised water. Transfer to the relevant instrument container. Store at room temperature for up to 3 months.

7.5 Baseline Solution

Slowly, quantitatively transfer 0.8 ± 0.05 g of sodium hydroxide into a 2000 ml volumetric flask containing approximately 1500 ml deionised water. Mix to dissolve and make up 2000 ml mark. Add 2 ± 0.1 ml of the sodium thiosulphate 2.5 % w/w

solution. Transfer to the instrument container designated as ‘Baseline’. Store at room temperature for up 1 month.

7.6 Wash Solution

Slowly, quantitatively transfer 1 ± 0.05 g of sodium hydroxide into a 250 ml volumetric flask containing approximately 200 ml deionised water. Mix to dissolve. Quantitatively transfer 18.8 ± 0.1 g of potassium chloride. Mix to dissolve and make up to 250 ml mark with deionised water. Transfer to the instrument container designated as ‘WASH’. Store at room temperature for up to 3 months.

7.7 1M Sodium Hydroxide Solution

Quantitatively transfer 20 ± 1 g of sodium hydroxide into a 500 ml volumetric flask containing approximately 300 ml deionised water. Mix to dissolve and make up to the mark with deionised water. Store the solution for up to 1 year.

## 8 Calibration Solutions

A complex cyanide stock standard of 1000 mg/L is required.

8.1 Total Cyanide Intermediate Standard, 10 mg/L

Pipette 1000 µl of Stock Calibration standard and 1000 µl of 1M Sodium Hydroxide solution into a 100 ml volumetric flask, containing approximately 50 ml deionised water. Make up to the mark with deionised water and mix. Prepare fresh for each batch.

8.2 Total Cyanide Intermediate Working Standard, 1 mg/L

Using the appropriate auto pipette, transfer 5000 µl of Intermediate Calibration Standard (8.1) into a 50 ml volumetric flask, containing approximately 25 ml deionised water. Make up to the mark with deionised water and mix. Prepare fresh for each batch.

8.3 For the calibration, add to a series of 50 ml volumetric flasks, 0, 250, 500, 1000, 1500, 2000, 2500 and 3000 µl of total cyanide Intermediate Working Standard (8.2). Add to each flask 50 µl of 2.5% w/w Sodium Thiosulphate Solution (7.1) and 500 µl of 1M Sodium Hydroxide solution (7.7) and make to volume with water. These flasks now contain 0, 5, 10, 20, 30, 40, 50 and 60 µg/l of cyanide respectively. These solutions should be prepared fresh for each batch.

## 9 Apparatus

Suitable segmented flow apparatus with on-line UV digestion and gas diffusion amperometric detector with autosampler and equipped with a data acquisition system is available commercially.

Acid and Basic waste receptacles are kept separate. This is to ensure that there are no accidental gaseous releases of hydrogen cyanide by acidification of the basic waste containing dissolved cyanide ion. Waste shall be emptied as soon as possible after each analytical run.

The unit must be equipped with a peristaltic pump, a mixing coil, an UV digester unit a manifold for the hydrophobic gas diffusion membrane and a measuring silver electrode; silver/silver chloride reference electrode and a counter electrode.

It is important that measures are followed to prevent the membrane manifold/electrode housing from drying when the system is not operating. The waste line must be clipped when the system is not running, or the basic reagent flow must be kept recirculating continuously on a pulsing mode.

The system can perform onboard serial dilutions to generate the calibration standards. This is optional. The analytical procedure does not describe this step.

## 10 Analytical Procedure

10.1 Following the manufacturer's general operating instructions, set up the instrument ensuring all reagents are correctly connected in series. Ensure there is sufficient available reagents to avoid having to replenish any reagent during the analytical run.

10.2 With the sample probe at rest in the wash receptacle solution and all on-line reagents tubes in DI water, unclip the basic waste line. Fit the tubes on the peristaltic pump both on the analyser and the autosampler. Switch the power on, on the analytical unit and autosampler. Allow for equilibration time and perform a wash of the lines. Check the bubble pattern and hydraulic behaviour is uniform.

10.3 Remove the tubes from all on-line reagents from DI water and place the tubes for each of the reagents in the appropriate container. Allow for further suitable equilibration until an acceptably smooth baseline trace is given at the measurement unit.

10.4 The baseline response is pre-defined at 5 per cent of full scale. Adjust on the software the signal to this level. The system can then be calibrated. Drift is the most common issue encountered. It is important to define the typical baseline in each system and monitor against it.

10.5 Load the turntable with suitable calibration, blank, controls, samples and wash solutions (this can be done during the initial stabilisation period). Calibrate from the highest to lowest calibration standard. The system requires a first strong signal in the detector to determine the reading times of the subsequent samples. This is best achieved with the top calibration standard. The top calibration standard can be setup to be read more than once at the start of the run to prime the detector’s response if required.

10.6 When a steady baseline is obtained on the measurement unit, re-adjust it to about 5% of full scale. The set point at 85% of the full scale should be 3.7 to 4 greater than the µA value of the baseline on the Y axis. This adjusts the magnitude of the signal on the graph.

10.7 Adjust the baseline by setting the discriminator back to zero. The sequence can be started.

10.8 When all the system responses of each individual solution/sample have appeared as peaks on the graph and a final baseline has been obtained, the sequence will terminate. Flush all lines in DI water for at least 20 minutes, turn off the pump and release the pressure in the pump tubes, and clamp the detector channel to turn the system off. Alternatively, to reduce baseline instability between runs, recirculate the base reagent through the detector by keeping the pump running intermittently.

10.9 Plot a calibration curve of measurement unit responses (y-axis) against concentration (x-axis) of standard solutions. Using the calibration curve convert the measurement unit response due to the samples into concentration in the samples. Including any baseline and sensitivity change corrections.

**Table 1 Performance Data 0 – 20 µg/L Range**

| Nominal total cyanide concentration (in a 0-20 µg/L working range) (µg/L) | Total standard deviation (µg/L) | Degrees of freedom | Bias (µg/L) | Limit of quantification (µg/L) |
|---|---|---|---|---|
| 3 | 0.594 | 19 | 0.164 | 2.8 |
| 10 | 0.786 | 17 | 1.035 | |
| 18 | 0.915 | 24 | 1.368 | |

**Table 2 Performance Data 0 – 60 µg/L Range**

| Nominal total cyanide concentration (in a 0-60 µg/L working range) (µg/L) | Total standard deviation (µg/L) | Degrees of freedom | Bias (µg/L) | Limit of quantification (µg/L) |
|---|---|---|---|---|
| 10 | 1.084 | 16 | 0.950 | 6.5 |
| 30 | 1.728 | 14 | 1.296 | |
| 50 | 3.254 | 22 | 0.659 | |

**Table 3 Spike Recoveries of Matrices**

| Spike recoveries (50 µg/L fortification; in a 0-60 µg/L working range) | | | | |
|---|---|---|---|---|
| Treated Hard water | 99.7 | ± | 1.9 | % |
| Raw Ground Water | 100.5 | ± | 2.5 | % |
| Treated Soft water | 99.2 | ± | 2.0 | % |
| Raw Surface water | 102.3 | ± | 2.0 | % |

Commercially acquired stock standards of potassium tetracyano zincate salt used.

Data provided by Affinity Water Laboratory

## 11 References

1. Cheeseman R.V., Wilson A.L. NS30 A manual on analytical quality control for the water industry. (1989).

2. Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection. (2012). ASTM D7511-09e2.

3. Standing Committee of Analysts. The determination of cyanide in waters and associated materials. (2007). Methods for the Examination of Waters and Associated Materials.

4. Standing Committee of Analysts. The stability and preservation of drinking, ground and surface water samples. (2018). Methods for the Examination of Waters and Associated Materials.

5. Systea. Total Cyanide in water with amperometry. (2022). Method n. FLW-TCNamp-03rev.4.

**Members assisting with these methods.**

Without the good will and support given by these individuals and their respective organisations SCA would not be able to continue and produce the highly valued and respected blue book methods.

| | |
|---|---|
| Ana Rodrigues | Affinity Water Laboratories |
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| Alistair Gray | South West Water |
| Emma Thorpe | ALS Laboratories (UK) Ltd |
| Shaun Jones | mua Water |

## Correspondence

However well procedures may be tested, there is always the possibility of discovering hitherto unknown problems. Analysts with such information are requested to contact the Secretary of the Standing Committee of Analysts:

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## Amendment History

The determination of cyanide in waters and associated material using segmented flow with in-line UV digestion followed by gas diffusion amperometry is a new book. Therefore, there isn't an amendment history in this occasion.


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