Hydrazine in Waters Spectrophotometric Method 1981

Methods for the Examination of Waters and Associated Materials

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Spectrophotometric Method 1981

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Contents

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Warning to users

The analytical procedures given in this booklet should only be carried out by competent trained persons, with adequate supervision when necessary. Local Safety Regulations must be observed. Laboratory procedures should be carried out only in properly equipped laboratories. Field operations should be conducted with due regard to possible local hazards, and portable safety equipment should be carried. Care should be taken against creating hazards. Lone working, whether in the laboratory or field, should be discouraged. Reagents of adequate purity must be used, along with properly maintained apparatus and equipment of correct specifications. Specifications for reagents, apparatus and equipment are given in manufacturers' catalogues and various published standards. If contamination is suspected, reagent purity should be checked before use.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Code of Practice for Chemical Laboratories' and 'Hazards in the Chemical Laboratory' issued by the Royal Society of Chemistry, London; 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection', Public Health Laboratory Service Monograph 6, HMSO, London.

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radiochemical 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 part of a series intended to provide recommended methods for the determination of water quality. In addition, the series contains short reviews of the more important analytical techniques of interest to the water and sewage industries. In the past, the Department of the Environment and its predecessors, in collaboration with various learned societies, have issued volumes of methods for the analysis of water and sewage culminating in 'Analysis of Raw, Potable and Waste Waters'. These volumes inevitably took some years to prepare, so that they were often partially out of date before they appeared in print. The present series will be published as individual methods, thus allowing for the replacement or addition of methods as quickly as possible without need of waiting for the next edition. The rate of publication will also be related to the urgency of requirement for that particular method, tentative methods being issued when necessary. The aim is to provide as complete and up to date a collection of methods and reviews as is practicable, which will, as far as possible, take into account the analytical facilities available in different parts of the Kingdom, and the quality criteria of interest to those responsible for the various aspects of the water cycle. Because both needs and equipment vary widely, where necessary, a selection of methods may be recommended for a single determinand. It will be the responsibility of the users—the senior analytical chemist, biologist, bacteriologist etc, to decide which of these methods to use for the determination in hand. Whilst attention of the user is drawn to any special known hazards which may occur with the use of any particular method, responsibility for proper supervision and the provision of safe working conditions must remain with the user.

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is one of the joint technical committees of the Department of the Environment and the National Water Council. It has nine Working Groups, each responsible for one section or aspect of water cycle quality analysis. They are as follows:

1.0 General principles of sampling and accuracy of results
2.0 Instrumentation and on-line analysis*
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological methods
8.0 Sludge and other solids analysis*
9.0 Radiochemical methods.

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

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

Whilst an effort is made to prevent errors from occurring in the published text, a few errors have been found in booklets in this series. Correction notes for booklets in this series are given in the Reports of The Standing Committee of Analysts, published by the Department of the Environment but sold by the National Water Council, 1 Queen Anne's Gate, London SW1H 9TB. Should an error be found affecting the operation of a method, the true sense not being obvious, or an error in the printed text be discovered prior to sale, a separate correction note will be issued for inclusion in the booklet.

* These two working groups are in process of being wound up. Their tasks are being redistributed among the other Working Groups.

T A DICK
Chairman

L R PITTWELL
Secretary

25 September 1981

Hydrazine in Waters, Spectrophotometric Method 1981

1 Performance Characteristics of the Method

1.1	Substance determined	Hydrazine, N_2H_4.
1.2	Type of sample	Clean waters (d) (e).
1.3	Basis of method	p-Dimethylaminobenzaldehyde is added to the sample, and reacts with hydrazine to form a yellow azine, the concentration of which is measured spectrophotometrically.[1,2]
1.4	Range of application	Tested over the range 0–100 μg N_2H_4/litre.
1.5	Calibration curve	Linear to at least 100 μg N_2H_4/litre.

1.6 Total standard deviation

Sample Type	Concentration μg N_2H_4/litre	Standard Deviation μg N_2H_4/litre	Degrees of Freedom
Standard Solution	5	0.15–0.4 (a)	9
Standard Solution	100	0.45–1.7 (a)	9
Boiler Feed Water	8	0.32 (b)	9
Boiler Feed Water	44	0.36 (b)	9

1.7	Limit of detection (a)	0.4–1.0 μg N_2H_4/litre.
1.8	Sensitivity (c)	10 μg N_2H_4/litre–0.056 absorbence units.
1.9	Bias	No bias detected except when interferences occur.
1.10	Interferences	Substances normally present in high-purity waters do not interfere with the test (see Section 3.0). The hydrazine content may, however, be diminished by oxidizing agents collected with the sample or absorbed by it prior to testing.
1.11	Time required for analysis (b)	1 hour for 6 samples (total analytical time).

(a) Data from an interlaboratory exercise involving six Central Electricity Generating Board laboratories. All estimates had 9 degrees of freedom.
(b) Single laboratory's result (Data from the Central Electricity Generating Board).
(c) Data from the Central Electricity Generating Board.
(d) USEPA data[3] indicates that this method can also be used for at least some filtered effluents and river waters.
(e) Although hydrazine and its derivatives rarely occur in nature and it is readily oxidized, it can occur in some boiler water blow-downs, in effluents from some industries and spillage after transport accidents.[3]

2 Principle

The method is based upon the spectrophotometric measurement of the yellow azine formed by the reaction between hydrazine and p-dimethylaminobenzaldehyde.

3 Interferences

The effect of other substances in the determination is shown in Table 1.
The reagent p-dimethylaminobenzaldehyde is used for the determination of urea as well as hydrazine. However the 'urea azine' absorbance band (λ_{max}=420–430 mm) causes only a very small interference at the analysis wavelength of 455 nm for hydrazine. For example, although 50 mg/l urea gives an absorbance equivalent to 5 µg/l hydrazine, this concentration of urea is very unlikely to be present in normal boiler water blow-down. Oxidizing agents present in the sample or absorbed by it prior to testing will cause gradual decomposition of hydrazine at rates dependent on the nature and concentration of the oxidizing agent.

Highly coloured waters may interfere by absorbing at the same wavelength.

Substance added	Concentration, µg/litre	Effect in µg N_2H_4/litre at a hydrazine concentation of 0 µg/litre	10 µg/litre	100 µg/litre
Fe^{2+}	1,000	0.21	0.09	0.23
Cu^{2+}	1,000	0.04	—0.12	—0.47
Co^{2+}	1,000	—0.05	0.23	0.09
Ni^{2+}	1,000	0.21	0.18	0.18
Mn^{2+}	1,000	—0.18	—0.09	—0.21
Zn^{2+}	1,000	—0.23	0.23	—0.32
Ca^{2+}	10,000	0.18	0.58	—0.14
Mg^{2+}	10,000			
Fe^{3+} (a)	1,000	0.32	0.05	0.16
Fe^{3+} (a)	200	—	—	0.18
Al^{3+}	1,000	—0.35	—0.12	0.09
Cr^{3+}	1,000	—0.21	—0.35	—0.14
W (VI)	100	0.05	0.09	0.12
Mo (VI)	100			
Ti (IV)	100			
Sn^{4+}	100			
V (IV)	100			
SO_4^{2-}	100,000	0.44	0.56	0.39
PO_4^{3-}	100,000			
F^-	100,000			
NO_3^-	100,000			
Na^+	250,000			
K^+	150,000			
Ammonia	10,000	—0.35	0.26	—0.18
Cyclohexylamine	10,000	0.23	0.21	0.12
Morpholine	10,000	—0.14	0.12	0.12
Detergent (b)	1,000	0.05	0.12	0.61
95% confidence limits of each result if other substances had no effect		0.32	0.40	0.60

(a) If samples containing ferric ions and hydrazine are allowed to stand, the hydrazine concentration slowly decreases. For example, with 50 µg N_2H_4/litre and 1,000 µg Fe^{3+}/litre, the hydrazine concentration decreases by about 5 µg/litre after 30 hours.
(b) An alkyl-aryl sulphonate was used.
In this table the brackets indicate that the specified substances were present simultaneously in the test solutions.
Data in this table were obtained by the Central Electricity Generating Board.

4 Hazards

Hydrazine sulphate, solid and solution is used in this method, but the sample may contain the free base which is volatile and therefore more hazardous. Normal precautions to avoid skin contact and/or ingestion should be taken in the handling of all the reagents.

Hydrazine vapour should not be inhaled. Goggles and rubber gloves should be worn and contact with eyes, skin and clothing avoided.

Hydrazine can enter the body through the skin, lungs and, if ingested, through the digestive system. Severe over exposure may cause damage to the central nervous system, liver damage and haemolytic anaemia.

Repeated skin contact may in some cases lead to sensitization and skin breakdown on further exposure to very small quantities.

The vapour is irritating to the eyes, nose and throat, an effect that may take several hours to develop after exposure.

Hydrazine and hydrazine salts when fed in large quantities in laboratory experiments to small animals have been found to be carcinogenic. However, these experiments cannot be directly related to man and extensive studies of humans exposed to hydrazine or hydrazine salts do not indicate any evidence of an increase incidence of cancer. These investigations are continuing.

In the *Health and Safety Executive Guidance Note EH 15/78* the time weighted average exposure for an eight hour working day for hydrazine is set at 0.1 ppm and up to 0.3 ppm for a 15 minute period. The 15 minute exposure level should not be exceeded at any time. Levels between 0.1 and 0.3 ppm should not occur more than four times a day and there should not be less than 1 hour between such exposures; in addition the average for 8 hours should not exceed 0.1 ppm.

If the solution is concentrated, for instance, by evaporation to 40% hydrazine or more a severe explosive hazard arises on exposure to heat, oxidizing agents and strong acids. Spontaneous combustion can occur of rags or paper soaked in hydrazine. Solutions of hydrazine above 40% are combustible if heated sufficiently.

5 Reagents

Analytical reagent grade chemicals are suitable unless otherwise specified. Freshly boiled, distilled or de-ionized water should be used throughout.

5.1 p-Dimethylaminobenzaldehyde Reagent

Add 200±2 ml of hydrochloric acid (d_{20} 1.18) and 400±20 ml of water to a 1 litre glass beaker. Stir the contents of the beaker so that they are well mixed. To this solution, add 30±0.5 g of p-dimethylaminobenzaldehyde and stir until completely dissolved.

Transfer to a 1 litre amber coloured glass bottle fitted with a ground-glass stopper, and dilute with water to 1 litre (it is sufficiently precise to use a calibration mark on the bottle). This reagent is stable for at least 3 weeks if stored out of direct sunlight.

Some batches of p-dimethylaminobenzaldehyde may not dissolve completely. Insoluble matter should be filtered off before use.

5.2 Hydrochloric acid, 2M

Carefully add 200±10 ml of hydrochloric acid (d_{20} 1.18) to about 700 ml of water and dilute to 1 litre with water in a measuring cylinder.

5.3 Hydrochloric acid, about 0.4M

Dilute 20±1 ml of hydrochloric acid, reagent 5.2, to 100 ml with water in a measuring cylinder.

5.4 Stock Standard Hydrazine Solution 1 ml = 50µg Hydrazine

Add 10±1 ml of hydrochloric acid (d_{20} 1.18) and about 800 ml of water to a 1 litre calibrated flask. Wash into the flask 0.203±0.0005 g of hydrazine sulphate ($N_2H_6.SO_4$) and shake until completely dissolved. Dilute to the mark with water. Store the solution in a glass bottle with a ground-glass stopper. Any change in the hydrazine content of this solution has been found to be less than 1% over a period of 3 months.

5.5 Working Standard Hydrazine Solution 1 ml = 0.2 µg Hydrazine

Pipette 2.0±0.02 ml of stock solution 5.4 into a 500-ml calibrated flask and dilute to the mark with water. Store the solution in a glass bottle with a ground-glass stopper. This solution should be prepared freshly each week.

6 Apparatus

6.1 A Spectrophotometer capable of operating at 450–460 mm with 40 mn path-length cells.

6.2 Clean 50-ml calibrated flasks by soaking them and their stoppers overnight in chromic acid cleaning solution. Wash copiously first with tap water and then with distilled water. Carry out steps 9.5–9.6 in each flask and discard the solutions without measuring their absorbances. The flasks should now be adequately clean for sample analyses.

A set of cleaned flasks should be reserved solely for hydrazine determinations.

6.3 Borosilicate-glass Sampling Bottles

These bottles, which should have ground-glass stoppers, may be of any convenient size. Clean the bottles and stoppers as in Section 6.2. The bottles should now be adequately clean for collecting samples.

6.4 Water bath at 25±1°C.

7 Sampling and Sample Storage

Add sufficient hydrochloric acid (d_{20} 1.18) to the bottle in which the sample is to be collected, so that the final acid concentration when the sample has been collected will be 0.01±0.001M.

The temperature of the water emerging from the sampling device should not exceed 30°C. When the sample has been collected, insert the stopper in the bottle. If possible avoid trapping air beneath the stopper.

The stability of the acidified sample depends on the other consituents (eg iron) present. Samples should be analysed as soon as possible after sampling and should not be stored for more than 24 hours.

8 Calibration Procedure

8.1 Into a series of dry 50 ml graduated flasks place 0.20±0.02 ml of 2M hydrochloric acid (Reagent 5.2), and add, by means of a burette the volumes of working standard hydrazine solution shown in the table below.

Volume of solution 5.5 (ml)	Mass of hydrazine (µg)
0.00	0
2.00	0.4
4.00	0.8
8.00	1.6
12.00	2.4
16.00	3.2
20.00	4.0

8.2 Add water by means of a burette to each flask to give a volume of 40±0.1 ml.

8.3 Continue as under Procedure steps 9.2 and 9.4.

8.4 Subtract the absorbance of the blank solution from the absorbances for all the other standards and plot a calibration graph of µg hydrazine versus absorbances. This is normally linear and passes through the origin.
For measurement at 455 nm, the slope of the calibration curve decreases by about 1 % for an increase in temperature of 1°C over the range 15–25°C.
The curve should be checked for each series of tests, by running two or more solutions of known hydrazine concentration.

9 Analytical Procedure

Step	Experimental Procedure	Notes
	Analysis of samples	
9.1	Pipette 40 ml of acidified sample (7.0) into each of two dry 50 ml calibrated flasks. Denote the flasks as 'sample' and 'sample blank' (note a).	(a) The 'sample blank' may be omitted if it is known that the absorbance from suspended matter/colour is negligibly small.
9.2	Add 10.0±0.1 ml of p-dimethylaminobenzaldehyde reagent to the 'sample' flask. Insert the stopper, mix the contents of the flask and place in a bath of water at 25±1°C for 10±5 minutes (note b). Measure the absorbance A_s, as in step 9.4.	(b) The intensity of the yellow colour of the azine depends on the temperature of the solution.
	Preparation of Sample Blank	
9.3	Add 10±0.1 ml of 2M hydrochloric acid (5.2) to the 'sample-blank' flask. Insert the stopper, mix the contents of the flasks, and place in a bath of water at 25±1°C for 10±5 minutes. Measure for absorbance A_d as in step 9.4.	
9.4	Set up the spectrophotometer according to the manufacturer's instructions. Adjust the zero of the instrument with 0.4M hydrochloric acid reagent (5.3) in the reference cell (note c). Measure the absorbance of the solution at 455 nm (note c). Recheck the intrument zero.	(c) Use 40 mm cells. The wavelength of maximum absorbance should be checked for each individual instrument. This wavelength should be used for all subsequent measurements.
	Preparation of Reagent Blank (note d)	
9.5	Add 0.20±0.02 ml of 2M hydrochloric acid (5.2) and 35±2 ml of water to a 50 ml calibrated flask denoted 'reagent blank'. Insert the stopper and mix the contents of the flask.	(d) A reagent blank must be run with each batch of analyses.
9.6	Proceed as in step 9.2. Measure the absorbance A_b as in step 9.4.	

10 Calculation

Calculate the absorbance (A_r) due to hydrazine in the sample from:

$$A_r = A_s - (A_b + A_d)$$

Determine the mass of hydrazine (M) in the sample from A_r and the calibration curve.

Neglecting the very small error from the acid added to the sample, the hydrazine concentration = 25M µg/l.

11 References

(1) Pesez and Petitt, *Bull. Soc, Chim.* France, 1947, p. 122,

(2) Watt and Chrisp, *Anal. Chem.*, 24, 1952, p. 2006.

(3) *J. Water Pollution Control Federation*, May 1981, p. 568.

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However thoroughly a method may 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:

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