Colour and Turbidity of Waters 1981

Methods for the Examination of Waters and Associated Materials

London: Her Majesty's Stationery Office £2.75 net

Colour and Turbidity of Waters 1981 Tentative Methods

Methods for the Examination of Waters and Associated Materials

This booklet contains three methods for the determination of colour and two methods for the determination of turbidity. The methods described cater for the variety of field and laboratory needs that arise requiring these determinands.

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 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; 'Safety in Biological Laboratories' (Editors Hartree and Booth), Biochemical Society Special Publication No 5, The Biochemical Society, London, which includes biological hazards; and 'The Prevention of Laboratory Acquired Infection, 'Public Health Laboratory Service Monograph 6, HMSO, London.

Where the Committee have considered that a special unusual hazard exists, attention has been drawn to this in the text so that additional care might be taken beyond that which should be exercised at all times when carrying out analytical procedures. It cannot be too strongly emphasised that prompt first aid, decontamination, or administration of the correct antidote can save life; but that incorrect treatment can make matters worse. It is suggested that both supervisors and operators be familiar with emergency procedures before starting even a slightly hazardous operation, and that doctors consulted after any accident involving chemical contamination, ingestion, or inhalation, be made familiar with the chemical nature of the injury, as some chemical injuries require specialist treatment not normally encountered by most doctors. Similar warning should be given if a biological or radio-chemical injury is suspected. Some very unusual parasites, viruses and other micro-organisms are occasionally encountered in samples and when sampling in the field. In the latter case, all equipment including footwear should be disinfected by appropriate methods if contamination is suspected.

The best safeguard is a thorough consideration of hazards and the consequent safety precautions and remedies well in advance. Without intending to give a complete checklist, points that experience has shown are often forgotten include: laboratory tidiness, stray radiation leaks (including ultra violet), use of correct protective clothing and goggles, removal of toxic fumes and wastes, containment in the event of breakage, access to taps, escape routes, and the accessibility of the correct and properly maintained first-aid, fire-fighting, and rescue equipment. Hazardous reagents and solutions should always be stored in plain sight and below face level. Attention should also be given to potential vapour and fire risks. 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.

First published 1984

ISBN 0 11 751955 3

About this series

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

The preparation of this series and its continuous revision is the responsibility of the Standing Committee of Analysts (to review Standard Methods for Quality Control of the Water Cycle). The Standing Committee of Analysts is a committee of the Department of the Environment set up in 1972. Currently it has seven 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
3.0 Empirical and physical methods
4.0 Metals and metalloids
5.0 General nonmetallic substances
6.0 Organic impurities
7.0 Biological methods
9.0 Radiochemical methods.

The actual methods and reviews 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.

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 and minor additions to published booklets not warranting a new booklet in this series will be issued periodically as the need arises. 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 that booklet.

L R PITTWELL
Secretary

31 October 1983

A Methods for the Measurement of the Colour of Raw and Potable Waters and Effluents

Introduction

When viewed by transmitted light through a depth of several feet, pure water exhibits a light blue colour which may be modified by the presence of organic matter to greenish blue, green, greenish yellow, yellow or brown. For analytical purposes "true colour" may be described as that due to dissolved matter. "Apparent colour" is that which is seen in the presence of suspended matter in the sample. The colour of some waters may be affected by pH[5]. Some substances fluoresce and care is necessary to distinguish between the colours due to absorption and fluorescence. The latter is best observed at right angles to the incident light. Turbidity in excess of 1 NTU (nephelometric turbidity unit — see Determination of Turbidity, also included in this booklet) seriously affects colour determinations, the "apparent colour" in its presence being higher than the "true colour". To obtain the true colour intensity in these circumstances it is necessary to filter the sample through a cellulose acetate membrane. Samples containing dissolved iron may become turbid subsequent to collection and analysts should be aware of this phenomenon.

Selection of method

Three methods are described namely:

1 Simple determination of colours

2 Visual method for the determination of colour

3 Instrumental measurement of colour by absorbance.

The "simple method" is essentially an on-site or field method. It may also be used when simple colours are not capable of being matched with normal standard colours. The visual comparison method is the method of choice for routine control in the laboratory when samples are roughly in the right shade range.

The instrumental method is a reproducible method mainly used in investigation work and for the studying of long term trends. It can however be used as an alternative to the visual comparison method for routine use. Results obtained by the two methods do not exactly agree although a correlation exists (see Instrumental method, Section A3.11).

A.1 Simple Determination of Colour

A1.1 Performance Characteristics of the Method

The method is purely qualitative and highly subjective. Accuracy and Precision data are therefore not available. It is suggested that analysts carrying out this method be given a colour vision test to eliminate errors due to defective vision. As colour vision can vary with age, this test may need repeating occasionally.

A1.2 Principle

The colour is assessed by eye, if necessary, after preliminary filtration.

A1.3 Field of Application

The method is applicable to all waters and effluents.

A1.4 Interferences

Colour can be due to suspended fine particles as well as a true solution, and colloids.

Colour can change with pH.

A few dyes are absorbed by filter paper.

A1.5 Apparatus

A1.5.1 Clear colourless glass bottles.

A1.5.2 A white background, illuminated by north light, or equivalent.

A1.5.3 If necessary, filter funnels with qualitative grade filter paper (preferably fluted for rapid filtration) or similar device.

A1.6 Sample Collection and Preservation

See section A2.7.

A1.7 Analytical Procedure

Step	Procedure	Notes
A1.7.1	Shake the sample well in a stoppered clear glass bottle.	
A1.7.2	If necessary, filter through a qualitative grade filter paper into another similar bottle (a)(b).	(a) Examine the filter paper to check whether the colour is due in part to suspended matter. Note also whether, due to absorption of colour, the used paper, clear of any solid is of darker hue than the filtrate. (b) With some coloured waters it may be worth noting whether a beam of light shone through the filtrate shows a pronounced cone (Tyndal's cone effect) due to colloidal matter present.
A1.7.3	Examine the sample visually against a white background in a north light, and describe the colour and classify accordingly to colour intensity. Typical Intensities and Descriptions are listed below (c).	(c) Colourless and Black cannot have intensities. White solutions are often turbid and some other intensity term may be more apt. Black solutions often exhibit another colour in addition, which may be noticeable on the filter paper. If so, note this fact. (d) Avoid obscure or ambiguous terms.

Intensity	Description	
Very Pale	Colourless	Orange
Pale	White	Yellow
Dark	Grey	Straw
	Black	Green
	Brown	Blue
	Red	Others (Specify)(d).

A2 Visual Method for the Determination of Colour Tentative method

A2.1 Performance Characteristics of the Method

A2.1.1	Substances determined	Visually detectable colour after removal of any turbidity.
A2.1.2	Types of sample	Raw and potable waters.
A2.1.3	Basis of the method	Visual comparison of colour intensity, under specified conditions, against inorganic colour standards or calibrated permanent glass standards.
A2.1.4	Range of application	Up to 70 Hazen units.
A2.1.5	Standard deviation	Not determined, see Section A2.1.8.
A2.1.6	Limit of detection	The method as described is applicable down to 5 Hazen units for standard comparison tubes. Lower values, depending on the colour sensitivity of the analyst, can be obtained using longer tubes (see step A2.8.4 note b).
A2.1.7	Sensitivity	Depends on the analyst's ability to match colour.
A2.1.8	Bias	Not known.
A2.1.9	Interferences	Turbidity greater than 1 NTU using the formazin standard as defined in the method for turbidity (but see step A2.8.2 note a).
A2.1.10	Time required for analysis	About 3 minutes per sample, excluding any filtration and the periodic preparation of standards.

A2.2 Principle

Colour is expressed in terms of the 'Hazen' standard unit, which is defined as the colour produced by 1 mg/l platinum in the form of chloroplatinic acid in the presence of 2 mg/l of cobaltous chloride hexahydrate.

The intensity of the colour is measured by visual comparison against a series of standard Hazen solutions or against permanent glass standards.

A2.3 Field of Application and Interferences

The method is applicable to raw and potable waters. Finely divided suspended matter interferes in the measurement and must be removed by filtration before the comparison is made against the standards (step A2.8.2 note a).

A2.4 Hazards

No specific hazards other than those normally associated with the use of laboratory chemicals and apparatus.

A2.5 Reagents

Analytical reagent grade chemicals should be used unless otherwise specified.

A2.5.1 Water

Distilled or deionized is suitable.

A2.5.2 500 Hazen units stock solution (a)

Dissolve 1.245 ± 0.001 g potassium chloroplatinate (K_2PtCl_6) and 1.000 ± 0.001 g cobaltous chloride hexahydrate ($CoCl_26H_2O$) in about 500 ml of water. Add 100 ± 1 ml of hydrochloric acid (d_{20}1.18) and dilute with water to 1 litre in a calibrated flask. The colour of this solution is 500 Hazen units.

Store the solution in a well stoppered glass bottle in the dark at a temperature not exceeding 30°C. This solution will normally remain stable for at least six months.

A2.5.3 Hazen standards (a)

Prepare a series of standards, having a range of 5 to 70 Hazen units, by suitable dilutions of the stock solution with water to 250 ml in calibrated flasks.

Store the standards in well stoppered glass bottles in the dark at a temperature not exceeding 30°C.

Check the storage stability of the standards at monthly intervals by visual comparison (step A2.8.4) of the colour of the 10 Hazen units standard with that of a freshly prepared standard. If the intensity and shade of the solutions are identical, store the series of standards for a further month and then re-examine. If precipitation is detected in the standards or if the intensity or shade of the stored standard differs from that of the freshly prepared standard, dispose of the stored standards and prepare a fresh series by appropriate dilution of the stock solution.

Permanent glass standards covering a similar range of Hazen units are commercially available. Their use is permissible provided that they are checked at three-monthly intervals against standard Hazen solutions and recalibrated if necessary. The calibration of the glass standards is only valid when they are used in the type of apparatus specified by the manufacturer, using the size of tube recommended.

The glass standards must be re-calibrated against standard Hazen solutions if longer, non-standard tubes are used for the comparison.

A2.5.4 20% V/V Hydrochloric acid

Dilute 200 ± 2 ml of hydrochloric acid (d_{20}1.18) with water to 1 litre in a measuring cylinder. Store in a polyethylene or borosilicate glass bottle.

A2.6 Apparatus

A2.6.1 Cellulose Acetate Membrane — 0.45 μm effective pore diameter.

A2.6.2 Standard Observation Tubes — 50 ml, calibrated and optically matched, Nessler tubes.

A2.6.3 Special Observation Tubes — Longer, non-standard tubes (step A2.8.4 note b).

A2.6.4 Cleaning of Apparatus — Clean the observation tubes by washing thoroughly with a suitable commercially available, detergent or with 20% V/V hydrochloric acid. Rinse well with distilled or deionized water before use.

Glass standards must be clean and free from grease and dust. Avoid touching the faces and if necessary clean according to the makers' instructions.

(a) It is often possible to return discarded platinum compounds for partial credit. For advice on the most acceptable form and quantity consult refiners, listed in the trade indexes.

A2.7 Sample Collection and Preservation

Collect samples in glass stoppered bottles cleaned as described in Section A2.6.4 and carry out the colour test as soon as possible after collection. If storage is unavoidable, store the samples in the dark at ambient temperature.

A2.8 Analytical Procedure

Step	Procedure	Notes
A2.8.1	Fill a series of nine standard observation tubes to the calibration mark with Hazen standard solutions. Range of colour standards required is 5, 10, 15, 20, 30, 40, 50, 60 and 70 Hazen units.	
A2.8.2	Fill a standard observation tube with sample (note a).	(a) If the turbidity of the sample is greater than 1 NTU, filter through a cellulose acetate membrane and measure the colour of the filtrate. In the presence of clay or other finely suspended matter it may not be possible to obtain a bright filtrate. In these circumstances only 'apparent' colour can be measured.
A2.8.3	Place the observation tubes over a white surface placed at such an angle that north light or light from a whitelight cabinet is reflected upwards through the columns of liquid.	
A2.8.4	Look vertically downwards through the columns of liquid. Match the intensity of the colour of the sample with that of the nearest Hazen standard (note b).	(b) If the intensity of colour of the sample exceeds 70 Hazen units dilute with water in known proportions until it is within the range of the standards and multiply by the appropriate factor. If colours less than 5 Hazen units are to be measured, longer observation tubes may be used with the appropriate Hazen standards.
	Results	
A2.8.5	Record the value of the colour to the nearest 5 Hazen units (note c and d).	(c) If the colour of the sample does not match that of the Hazen standards, an approximate value is reported with an appropriate note. (d) If matching is impossible, give a description of the colour of the sample.

A3 Instrumental Measurement of Colour by Absorbance Tentative method

A3.1 Performance Characteristics of the Method

A3.1.1	Substance determined	Absorbance at a wavelength of 400nm in 40mm cells, after filtration through a 0.45 μm filter.
A3.1.2	Type of sample	Raw and potable waters and certain effluents (see Section A3.3).
A3.1.3	Basis of method	Measurement of absorbance of the sample in 40mm cells at a wavelength of 400nm after filtration through a 0.45 μm filter.
A3.1.4	Standard deviation (within-batch)(a)	Absorbance range / Standard Deviation / Degrees of freedom 0–0.03 absorbance units / 0.0007 absorbance units / 53 0.03–0.06 absorbance units / 0.0011 / 9
A3.1.5	Detection limit	0.007 absorbance units with 44 degrees of freedom (b).
A3.1.6	Sensitivity	Depends on the instrument scale.
A3.1.7	Interferences	No tests have been made.
A3.1.8	Bias	Not known.
A3.1.9	Time required for analysis	The total analytical and operator times are the same and are highly dependent on the rate of filtration of the samples. Typical times for 1 and 10 samples are 25 and 75 minutes.

Notes:

(a) These figures are based on the difference between duplicate measurements on samples of different absorbances in the stated ranges made on different days by the Water Research Centre, Medmenham.

(b) This figure is based upon the measurement made by the Water Research Centre, Medhmenham; on different days, of the absorbance of filtered deionized water using unfiltered water from the same batch as reference. The assumption is made that filtration does not affect the measured absorbance.

A3.2 Principle

The sample is filtered through a cellulose acetate membrane of 0.45 μm pore size and the absorbance of the filtrate measured spectrophotometrically in 40mm cells at 400nm. The result is expressed in absorbance units.

A3.3 Field of Application

This method is applicable to the measurement of raw and potable waters and some effluents. In the latter case, it is advisable to measure the spectrum of the sample in the visible wavelength region and to measure the absorbance at the wavelength of maximum absorption. The wavelength should be quoted with the result.

A3.4 Interferences

None. Occasionally a spectrophotometer may have a defective monochromator. New instruments should be checked and if defective rejected. Proper care and maintenance should ensure continued accuracy.

A3.5 Hazards

Care must be taken when handling acids, particularly chromic acid. Eye protection, gloves and protective clothing should be worn.

All apparatus used for vacuum filtration should be inspected for flaws and star-cracks before use. Ideally, vacuum filtration should be carried out behind a safety screen. Alternatively the glassware can be covered with a suitable protective mesh.

A3.6 Reagents

Analytical grade reagents and deionized or distilled water are used throughout unless stated otherwise. All reagents and solutions should be kept in borosilicate glass bottles.

A3.6.1 2.5M Sulphuric acid (approximately)

Add 140 ± 2 ml sulphuric acid (d_{20} 1.84) cautiously to about 800 ml of water in a 2-litre beaker stirring and cooling the solution. Transfer to a measuring cylinder with water. Allow to cool and dilute with water to 1 litre.

A3.6.2 Control solution (see Section A3.12)

Dissolve 0.200 ± 0.001g potassium dichromate in water and dilute to 250ml in a volumetric flask. Pipette 10.00 ± 0.04 ml into a 2–litre calibrated flask, add 10 ± 1ml of 2.5M sulphuric acid and dilute with water to the mark.

A3.6.3 Control solution reference water (see Section A3.12)

Store 2 litres of the water used to prepare the control solution.

A3.6.4 Chromic acid cleaning solution

Dissolve 70 ± 1g technical grade sodium dichromate in the minimum amount of water in a 2–litre borosilicate glass beaker. Add cautiously 1 litre of sulphuric acid (d_{20} 1.84) to the solution, stirring thoroughly but with care. Allow any precipitate to settle and decant into a glass bottle. This solution is a powerful oxidizing agent and must be used with care.

A3.6.5 Dilute chromic acid cleaning solution

Add 100 ± 5 ml of the chromic acid cleaning solution carefully and with stirring to about 700 ml water in a borosilicate glass beaker and dilute with water to 1 litre in a measuring cylinder when cool.

A3.6.6 Hydrochloric acid 20% V/V

Dilute 200 ± 2 ml hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder.

A3.7 Apparatus

A3.7.1 A spectrophotometer equipped with a set of 40 mm cells.

Borosilicate glass filtration apparatus suitable for 47 mm filters
Buchner flasks of 250–ml capacity.

Cellulose acetate membrane filters, 47 mm diameter and effective pore size 0.45 μm.

A source of vacuum such as that provided by a water pump.

A3.7.2 Cleanliness

Maintenance of laboratory glassware in scrupulously clean condition is of utmost importance. Store the base of the filter holder in an inverted position with the neck full of dilute chromic acid, and the Buchner flask filled with 20% V/V hydrochloric acid. Before use pour the cleaning solutions away and thoroughly rinse with water.

Reagent bottles should be cleaned with a 2% V/V solution of a laboratory surfactant, rinsed with 20% V/V hydrochloric acid and thoroughly rinsed with water prior to use.

Store the spectrophotometer cells in a 2% V/V solution of a laboratory surfactant. Empty and rinse thoroughly with water prior to use. Polish the optical surfaces of the cells with an optical polishing cloth.

A3.8 Sample Collection

Collect the samples in borosilicate glass bottles which have been previously cleaned with dilute chromic acid cleaning solution and thoroughly rinsed with water. Rinse the bottle two or three times with sample before filling.

The samples must be analysed as soon as possible after collection.

A3.9 Analytical Procedure

Step	Procedure	Notes
A3.9.1	Assemble the filtration apparatus without a membrane filter and pass two portions of about 200 ml of water through the sinter. Discard the washings.	
A3.9.2	Insert a membrane filter. Filter about 50ml of the sample and discard the filtrate. Filter a further 50 to 70ml and retain in a beaker covered with a watchglass (notes a and b).	(a) Apply gentle vacuum (2.6–3.3kPa) to speed filtration. (b) Rinse out the beaker twice with filtered sample.
A3.9.3	Switch on the spectrophotometer; set the wavelength to 400nm (note c.)	(c) Refer to the instrument operating instructions. The analyst should assure himself that the wavelength of the instrument is accurately calibrated as a slight error in wavelength can cause a substantial error in absorbance.
A3.9.4	Fill the spectrophotometer cells with deionized water and measure the cell difference, A_C using one cell as reference. Record the values in absorbance units (notes d and e).	(d) If a double beam spectrophotometer is used, one cell should be placed in the reference beam. It is helpful to mark the cells with a pencil on the ground faces and always use the same cell for reference. The cell difference can be compared with previous values to ensure that no contamination has occurred. The cells should always be placed in the holders with the same optical face directed at the source. If more than one sample cell is used, each cell difference must be measured.
A3.9.5	Fill the sample cell with filtered sample (note e).	(e) Always empty and refill cells three times prior to measurement.
A3.9.6	Measure and record the absorbance A_s Correct for cell difference: Result = $(A_S - A_C)$	
A3.9.7	Report as absorbance at 400nm in 40mm cells (note f).	(f) Results may also be expressed in absorbance per metre. $(A_S - A_C)\frac{1000}{40}$
	Contamination Check (note g)	
A3.9.8	After washing the filtration apparatus (step 9.1), insert a membrane filter, filter about 50ml of water and discard the filtrate. Filter a further 50–70ml and retain in a beaker covered by a watchglass.	(g) It is recommended that this procedure be carried out regularly. It provides a check against possible contamination by residual cleaning agents or other contaminants.
A3.9.9	Measure the absorbance using water from the same batch which has not been filtered as reference. Correct for cell difference (note h).	(h) Contamination is indicated if the result exceeds about 0.003 absorbance units. The construction of an analytical quality control chart is recommended as an aid in assessing whether contamination has occurred.

A3.10 Sources of Error

Contamination from the use of unsatisfactorily cleaned laboratory glassware, is a possible source of error.

Filter colorimeters can give results which do not agree with those obtained using a spectrophotometer. The use of instruments of differing band pass may also give results which differ, but to a lesser extent.

The spectra of certain natural dissolved species in water are pH dependent.[5] Wilson[1] has reported the variation of absorbance with pH for fulvic acid at 300nm. It is recommended that the pH of samples should be quoted with colour measurements.

A3.11 Expression of Colour in Hazen Units

It is feasible to calibrate the spectrophotometer using Hazen standards ranging from 10 to 200 units. The standards are prepared by dilution of the stock Hazen solution described under visual measurement. It has been conclusively shown[2] that the results obtained by this procedure do not agree with those obtained visually, although a correlation exists. This is because the spectra of Hazen standards and of natural waters are different.

A3.12 Checking the Accuracy of Analytical Resources

One method suggested for overcoming this is to calibrate the spectrophotometer with natural water samples from a given source which have previously been analysed by the visual method. However it is not certain whether the agreement which is then attained by the two methods would be valid for different types of water.

It has also been shown[2] that the use of colorimeters equipped with filters gives results which differ from those obtained either visually or using a spectrophotometer. Moreover this is true whether the results are quoted as absorbance or as Hazen units after direct calibration of the instruments against Hazen standards. The results do, however, exhibit a linear relationship.

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[3,4]. For this method, three analytical quality control checks are proposed:

A3.12.1 Routine precision can be checked by calculating the difference between duplicate analyses on the same sample, at least one sample being analysed in duplicate in each batch. The results obtained should be plotted on a quality control chart which will facilitate detection of inadequate precision and will also allow the within batch standard deviation of routine analytical results to be estimated.

A3.12.2 Spectrophotometric accuracy can be checked by measuring the absorbance of the control solution against that of the control solution reference water. After making the cell corrections, the result is plotted on a control chart.

A3.12.3 The result of the contamination check (Sections A3.9.8 and A3.9.9) should also be plotted on a control chart.

B Turbidity

Introduction

Turbidity is an expression of the optical property of a liquid that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample.

It is used as a measure of the clarity of waters. The clarity is important both for aesthetic reasons and as a practical method for judging the effectiveness of water treatment processes such as filtration or flocculation. Turbidity is caused by suspended and/or colloidal material which is largely removed by modern water treatment processes and measurement of this parameter at various stages of treatment provides a useful method for works control.

Turbidity as measured is related to the physical characteristics of the substances in the sample. Correlation between this parameter and suspended matter determined gravimetrically is not normally possible since the scattering of light and hence the measured turbidity is affected by the particle size distribution, shape and refractive index of the suspended material.

The determination of turbidity has been accomplished by a variety of techniques. The traditional standard method was based on the Jackson standard candle turbidimeter which utilized the measurement of the length of a light path containing the water to be tested, through which was viewed a "standard candle". The length of the path at which point the image of the candle was extinguished was expressed as Jackson turbidity units (JTU).

The Jackson candle method is unsuitable for the examination of drinking waters. Attempts to use alternative procedures has resulted in confusion as there was little correlation between different instruments and different procedures.

Of the alternatives, two in particular have been favoured — the measurement of the reduction in intensity of transmitted light (absorptiometric methods) and the measurement of scattered light (nephelometric methods). Results from the two different techniques are not necessarily the same even on the same sample suspensions. The absorptiometric method is particularly susceptible to errors arising from the absorption of light by chemical species other than those responsible for turbidity, especially naturally occurring humic and fulvic acids which contribute to the colour of untreated waters. The method is less sensitive than nephelometry at low turbidities. Although some on line instruments are currently available which utilize the absorptiometric principle this method is not recommended as a standard laboratory procedure.

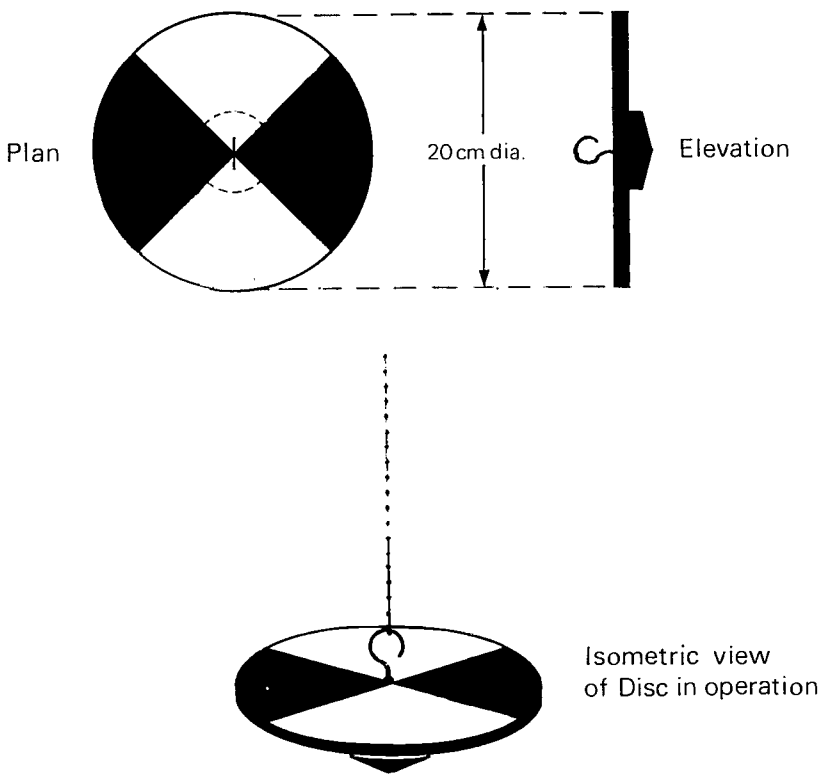
Nephelometric instruments, provided they are of similar design and measure light scattered at the same angle give results which are reasonably comparable between instruments. The method described attempts to overcome problems of non-comparability by specifying the precise details of instrument design. The use of the nephelometric technique largely overcomes the problem of interference caused by the presence of light absorbing species in the sample although the result may still be susceptible to some interference by colour. The results are expressed in nephelometric turbidity units (NTU) based upon the formazin standard prepared precisely as in Section B2.5 of the instrument method.

One of the major problems with any turbidimetric method is that of calibration. The use of standard suspensions for preparing calibration graphs will provide differing results if a variety of materials is used to make the suspension, since the turbidity as measured is dependent upon the wavelength of the incident light, the particle size, shape, colour and refractive index of the material. A number of substances have been used for this purpose including diatomaceous earth, fullers earth, kaolin, various clays, and latterly, a synthetic

suspension of formazin, an insoluble polymer formed by the condensation reaction between hydrazine sulphate and hexamethylenetetramine. Since the size, distribution and nature of the formazin suspension can be controlled accurately by specifying the conditions for preparation, this substance is becoming widely adopted as the turbidity standard.

One Formazin turbidity unit (FTU) is defined as $^1/_{400}$th of the turbidity of a formazin solution as prepared in Section B2.5.4 of the instrumental method, and a Nephelometric turbidity unit (NTU) is thus 1 FTU measured nephelometrically.

In addition to a laboratory method, a requirement exists for a method suitable for field use, particularly by those concerned with the study of waters in their natural state and for biological assessment. To meet this need a tentative method for turbidity using the Secchi disc is included. This procedure however, may not be a direct measure of turbidity and is best described as "the limit of visibility or transparency".



Secchi Disc

Figure 1

B.1 Determination of Turbidity (Secchi Disc Method) Tentative Method

B1.2 Performance Characteristics of the Method

B1.1.1	Substance determined	Visually detectable turbidity.
B1.1.2	Type of sample	Raw and river, lake and marine waters.
B1.1.3	Basis of Method	A Secchi disc is lowered into the water, the depth at which it disappears from view is noted, as is the depth at which is reappears on lifting. The average of these results is the limit of visibility.
B1.1.4	Range of application	Not known (a).
B1.1.5	Standard deviation	Not determined (a).
B1.1.6	Sensitivity	Depends upon observer, time of day, degree of roughness of water and clearness of the atmosphere.
B1.1.7	Bias	Not known (a).
B1.1.8	Interferences	Natural colour.
B1.1.9	Time required for analysis	Not more than 10 min per determination.

(a) The performance of the method is difficult to quantify as the reading is dependent not only on the amount of matter present, but on the particle size and the nature of the material. Normally, very small readings present greater difficulty and are less accurate and precise than larger readings, but observations as small as 2cm have been obtained under ideal conditions in lakes rich in very small unicellular algae or milk. With more floc-like material greater depths would be necessary. (See B1.5.1.1).

B1.2 Principle

Turbidity is defined by the "limit of visibility", or the depth of water at which a Secchi disc disappears from view when lowered into a body of water. Results are expressed in metres. The result is not an actual measure of light penetration but merely a useful index of visibility.

B1.3 Field of Application and Interferences

The method is applicable to sea waters, raw waters, and treated waters in some cases. It is of particular use for surface water inpoundments where measurements of turbidity are to be correlated with biological factors such as algal growth. Natural colour due to humic and fulvic acids may interfere.

B1.4 Hazards

There are no hazards associated with the method itself. Since the procedure is usually undertaken from a boat, precautions necessary for the safety of the occupants of the boat (eg lifejackets) must be taken.

B1.5 Apparatus

B1.5.1 Secchi disc consisting of a circular metal plate 20 cm in diameter the upper surface of which is divided into four equal quadrants and so painted that two quadrants directly opposite each other are black and the intervening ones white. A staple fixed at the centre of the upper surface provides attachment for a graduated rope. Opposite the staple on the

lower surface is a weight which facilitates the sinking of the disc. The lower surface of the disc is painted black in order to eliminate reflection of light from that surface. (Figure 1)

B1.5.2 Graduated rope. Nylon line 20 m in length, graduated by markers at 1 cm intervals for the first metre, and 10 cm intervals thereafter.

B1.5.3 Viewing box or tube with glass bottom for viewing through the water.

B1.5.A For very turbid waters where the extinction occurs in under 10–15 cm, a similar smaller disc 5–10 cm diameter held level by three equal threads to a common single string, may give better results. Calibration need only be in centimetres.

B1.6 Analytical Procedure

Step	Procedure	Notes
B1.6.1	Check that weather conditions and time are suitable (note a) and that the disc is not dull or scarred in any way (note b).	(a) Standard conditions require that the sun is directly overhead in a clear sky, with minimal waves or ripples on the water surface. Determination should only be made in the middle of the day, early morning and late afternoon must be avoided. (b) Frequent painting or enamelling of the disc is recommended.
B1.6.2	Lower the Secchi disc over the side of the boat using the side protected from any surface wind.	
B1.6.3	View the disc through a water telescope or glass bottomed box to avoid surface reflection problems. Lower the disc through the water and observe when it just disappears from view. Note the length of rope in the water (L_1 metre).	
B1.6.4	Continue lowering for 0.5 metre.	
B1.6.5	Raise the disc slowly, continuing to observe through the water telescope. Note the position of the rope when the disc just reappears (L_2 metre).	
B1.6.6	Calculation of results. The limit of visibility is $\frac{L_1 + L_2}{2}$ metres	

B2 Turbidity of Raw and Potable Water (Nephelometric Method) Tentative Method

B2.1 Performance Characteristics

B2.1.1	Substance determined	Turbidity resulting from suspended and colloidal matter in the sample.		
B2.1.2	Type of sample	Raw and potable water.		
B2.1.3	Basis of method	Nephelometry using formazin suspensions as the primary standards.		
B2.1.4	Range of application	Instrument dependent — typically with a modern instrument up to 100 NTU without dilution.		
B2.1.5	Standard deviation	Mean value NTU	Standard deviation NTU	Degrees of freedom
	Distilled water (a)	0.08	0.019	19
	Formazin standard (a)	4.01	0.010	19
	Formazin standard (a)	10.02	0.050	19
	Tap water (a)	0.54	0.014	19
	Raw water (a)	3.52	0.053	19
	Samples within turbidity range 0 to 1 NTU (b)		0.034	22
	Samples within turbidity range 1 to 10 NTU (b)		0.010	32
B2.1.6	Detection limit	Not determined.		
B2.1.7	Sensitivity	Depends on the instrument scale.		
B2.1.8	Bias	None known except for interference, see Section B2.1.9.		
B2.1.9	Interferences	No specific tests have been made but the presence of natural colour may lead to low results.		
B2.1.10	Time required for analysis	The operator and total analytical times are the same at less than 5 min per sample.		

(a) Within batch data obtained at Yorkshire Water Authority Head Office Laboratory using a Turner Designs nephelometer.

(b) The figures represent the pooled estimates of within-batch standard deviations based on the differences between duplicate measurements in samples of different turbidities within the stated ranges made on different days by the Water Research Centre using a Hach 2100 A nephelometer.

B2.2 Principle

Turbidity is an expression of the property by which suspended or colloidal matter scatters light thereby imparting opacity to the sample.

Light from a tungsten source, scattered by suspended and/or colloidal matter in the sample, is measured at right angles to the incident beam. The intensity of the light scattered by the sample is compared with that measured for standard formazin suspensions and expressed as nephelometric turbidity units (NTU).

B2.3 Interferences

Colour in the sample may give rise to low results depending on the particular instrument used. Although no specific tests of the quantitative effect of colour have been made, the effect is considered to be usually unimportant for treated waters, but each application needs individual consideration depending on the instruments used.

B2.4 Hazards

Avoid inhalation, ingestion and contact with the eyes and skin when handling both hydrazine sulphate and hexamethylenetetramine. Hydrazine salts when fed in large quantities in laboratory experiments to small animals have been found to be carcinogenic. However experiments cannot be directly related to man and extensive studies of human exposure to hydrazine salts do not indicate any evidence of an increased incidence of cancer. These investigations are continuing. Therefore hydrazine salts should be treated as possible carcinogens. Hexamethylenetetramine is a powerful diurectic.

B2.5 Reagents

Analytical grade reagents and specially-purified water are used throughout.

B2.5.1 Reagent Water

Filter a portion of distilled or demineralized water through a 0.1μm membrane filter, rejecting the first 200 ml. Store in a glass bottle in the dark. The filtration apparatus and bottle should be scrupulously clean; see Section B2.6.2.

Note: It has been reported that filtration of distilled water through a membrane filter may not reduce the turbidity reading and in some cases may increase its value.

B2.5.2 1.0% m/v Hydrazine sulphate solution

Dissolve 1.000 ± 0.001 g of hydrazine sulphate in water and dilute with water to 100 ml in a calibrated flask. Store in a glass bottle in the dark and discard after one month; see Section B2.4.

B2.5.3 10.0% m/V Hexamethylenetetramine solution

Dissolve 10.00 ± 0.01 g of hexamethylenetetramine in water and dilute with water to 100 ml in a calibrated flask. Store in a glass bottle in the dark and discard after one month; see Section B2.4.

B2.5.4 Stock Turbidity Standard: 400 NTU

Transfer 5.00 ± 0.03 ml each of hexamethylenetetramine and hydrazine sulphate solutions to a 100-ml calibrated flask. Mix well and allow to stand for 24 hr at 25 ± 3°C. Dilute with water to the mark and mix. Store in a glass bottle in the dark and discard after one month.

B2.5.4.1 Standard Turbidity Suspension: 40 NTU

Dilute 10.00 ± 0.04 ml of stock solution to 100 ml in a calibrated flask. Store in a glass bottle in the dark and discard after one week.

B2.5.5 20% V/V Hydrochloric acid

Dilute 200 ± 2 ml of hydrochloric acid (d_{20} 1.18) with water to 1 litre in a measuring cylinder. Store in a polythene or borosilicate glass bottle.

B2.5.6 Calibration Standards

Fresh, suitable calibration standards are prepared according to the required range of measurement. Some examples are given below:

Range of measurement NTU	Calibration Standard, NTU	Volume, ml of standard turbidity suspension per 100 ml final volume
0–1	1	2.5
1–10	10	25
10–40	40	Undiluted

B2.6 Apparatus

B2.6.1 Nephelometer

A nephelometer is required conforming to the specification given below. The use of instruments which deviate from this specification may lead to results *which differ from* those which would have been obtained using an instrument with the recommended specification. It is therefore desirable to use an instrument adhering to the following design considerations:

Light source:	Tungsten lamp operated at between 85 and 100% of rated voltage.
Light path:	The total distance travelled by incident plus scattered light within the sample should not exceed 10 cm.
Angle of light acceptance by director:	Not to exceed 30° and centred at right angles to the incident light path.
Measuring cells:	Glass cells.

B2.6.2 Cleanliness

All glassware must be kept scrupulously clean and it is recommended that it is cleaned by soaking in 10% V/V hydrochloric acid and thoroughly rinsed with deionized water prior to use. Maintenance of the measuring cells in a clean condition is essential. They must not be handled in the area where light strikes them and must be discarded if they become scratched.

B2.7 Sample Collection

Samples should be collected into glass bottles which have been thoroughly cleaned and rinsed with deionized water (see Section B2.6.2).

Samples should be analysed as soon as possible after collection. Turbidity may change rapidly on standing and checks should be made to ascertain the stability of different types of water. The permissible delay prior to examination will depend upon the nature of the sample being tested. Chemically stabilized samples should not be used.

B2.8 Analytical Procedure

Step	Procedure	Notes
B2.8.1	Switch on the nephelometer, allow it to warm-up and select a suitable measurement range (note a).	(a) Refer to the manufacturer's handbook for detailed operating and calibration instructions.
B2.8.2	Ensure that the appropriate calibration standard is well-mixed, rinse out the measuring cell and fill it. Adjust the range standardization control until the meter reads the correct value (notes b, c, and d). Ensure that any bubbles have risen to the surface (note e).	(b) In the absence of precalibrated scales, suitable calibration curves should be prepared by measurement of a range of suitable standards. Check the accuracy of any calibration scale supplied with the instrument in a similar way. (c) When checking the calibration of the low range, the turbidity of the reagent water should be ascertained so that a correction for stray light and the small scattering effect of the reagent water can be made (reading S). (d) "Permanent" secondary standards supplied with the instrument may be used provided that they have not deteriorated and are regularly checked against formazin standards. (e) The disappearance of air bubbles can be seen as an apparent decrease in turbidity after placing the sample tube in the instrument. A similar effect may be noted when coarse particulate matter settles-out.
B2.8.3	Allow the sample to come to room temperature and shake well. Rinse the measuring cell and fill it. Allow any air bubbles to rise (note e). Measure the turbidity (A).	

Step	Procedure	Notes
B2.8.4	For samples with turbidity greater than 40 NTU, prepare suitable dilutions using reagent water.	
B2.8.5	Calculation of results.	
B2.8.5.1	— for undiluted samples in 0–1 NTU range Turbidity = (A – S) NTU where A is the measured turbidity, S is the correction to be applied to the low range to compensate for stray light and the natural ability for the reagent water to scatter light (note c).	
B2.8.5.2	— for undiluted samples in the 1–40 NTU range Turbidity = (A) NTU where A is the measured turbidity.	
B2.8.5.3	— for diluted samples: $\text{Turbidity} = A\frac{(B + C)}{C}\text{NTU}$ where A is the measured turbidity, B is the volume of dilution water and C is the volume of sample.	

B2.9 Sources of Error

Erroneous data may result from several causes, the most likely being due to the use of dirty measuring cells or the presence of either air bubbles or rapidly-settling coarse particulates.

The presence of "true-colour" will cause absorption of light which may result in the measured values being low. Measurement of samples containing traces of oil should be avoided since this may foul the optical surfaces of the measuring cell.

It is recommended that samples with turbidities greater than the range of direct application of an instrument are measured after dilution with reagent water rather than by use of "cell risers" which effectively reduce cell path length. However, dilution may upset the sample equilibrium and it is possible that particulate matter may begin to dissolve, leading to low measured turbidities. Measurement must be made immediately after dilution.

B2.10 Checking the Accuracy of the Analytical Results

Once methods have been put into normal routine use, many factors may subsequently adversely effect the accuracy of the analytical results. It is recommended that experimental tests to check certain sources of inaccuracy should be made regularly. Many such tests are possible and should be used as appropriate.

For this method, it is proposed that routine precision should be checked by calculating the difference between duplicate analyses on the same sample, at least one sample being analysed in duplicate in each batch. The results obtained should then be plotted on a quality control chart which will facilitate detection of inadequate precision and also allow the within batch standard deviation of routine analytical results to be estimated. Additionally appropriate control solutions of formazin can be used as a check on the accuracy of results.

Further details of analytical quality-control procedures are given in standard texts such as those published by the Water Research Centre[3] and by the DOE Standing Committee of Analysts[4].

C Note on the Investigation of Colour and Turbidity Complaints

The procedures given in this booklet suffice for most quality control purposes in the Water Industry and Water Management. However, there may be occasions when it is necessary to quantify a colour more precisely. Several schemes based on absorption measurement at three or four wavelengths have been suggested related to the three colour effects associated with the human eye, but the only fool-proof scheme is the plotting of a wavelength-absorption curve using a prism or grating spectrophotometer with a narrow spectral bandpass (1–4 nm), which entails a narrow slit setting and a bright source lamp. For general scanning purposes wider settings may be tolerated. For more information see reference 6. If the colour of suspended solids or colloids is important a reflectance spectrophotometer may be used with either the filter used to filter the sample in steps A1.7.2, A2.8.2(a), A3.9.2 or a cell containing the sample mounted in the sample holder. See reference 7.

If a recording instrument is not available, make a preliminary plot from about 300 or 375 nm to 800 or 1000 nm at 15 to 20 nm intervals. Fill in fine detail by extra points at closer intervals, if necessary. Some substances, especially transition metal and lanthanide complex ions have very characteristic detail in their absorption peaks, for instance, the permanganate VII ion has twin peaks between 520–545 nm.

Estimation of the Accuracy of Analytical Results Using the Tentative Methods in this Booklet

Before firmly recommending the tentative 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 any of these methods could estimate the accuracy of its own analytical results and report the findings to the Secretary of the Empirical and Physical Methods Working Group* of the DOE Standing Committee of Analysts, together with full details of the precise method used.

The precision achieved is of particular interest. The value of this information would be greatly enhanced if it were obtained at the same determined concentrations as those for which some information has already been gained, as set out in the Performance Characteristics sections of these methods.

Similar information at other determined concentrations, and in sample types other than those already studied, would also be of great assistance. Detailed specifications for the tests to be carried out are beyond the scope of this booklet, but standard texts — such as those published by the Water Research Centre[3] and by the DOE Standing Committee of Analysts[4] — provide guidelines from which precision tests may be designed. The same texts also provide guidelines for interference and recovery tests and any information on these matters would be gratefully received.

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(4) *General principle of Sampling and Accuracy of Results 1980,* Methods for the Examination of Waters and Associated Materials, HMSO, London.

(5) *Ultra Violet and Visible Solution Spectrophotometry and Colorimetry 1980,* Methods for the Examination of Water and Associated Materials. HMSO, London. p7.

(6) Reference 5 whole booklet.

(7) *A Survey of Multielement and Retailed Methods of Analysis for Waters, Sediments and other Materials of Interest to the Water Industry 1980.* Methods for the Examination of Waters of Association Materials HMSO, London, Chapter 5.

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
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Printed in England for HMSO
Dd 736590 C12 6/84

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