

The Determination of Carbon Dioxide ² in Natural, Treated and Beverage Waters With a Supplement on Sampling Bottled and Canned Waters, 1986

Methods for the Examination of Waters and Associated Materials

The Determination of Carbon Dioxide in Natural, Treated and Beverage Waters With a Supplement on Sampling Bottled and Canned Waters, 1986

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This booklet consists of three parts, each containing several methods. The first part deals with natural waters, where the carbon dioxide content will normally be in equilibrium at atmospheric pressure. The second part deals with artificially carbonated and pressurized waters. The third part is a supplement dealing with the sampling of water in bottles, cans, syphons and containers for all determinands, but especially for carbon dioxide.

Part I, the Determination of Carbon Dioxide in Waters under Normal Atmospheric Pressure, contains a general introduction to the determination of free and total carbon dioxide in waters together with:

- A. A method for calculating carbon dioxide from the results of the determinations of sample alkalinity and pH value.
- B. A method for air strippable ("free") carbon dioxide and total carbon dioxide; and
- C. Reference to selective ion electrode methods for free and total carbon dioxide.

Part II, The Determination of Carbon Dioxide in Pressurized Bottled and Canned Waters, gives two methods for the determination of carbon dioxide in closed containers of mineral waters. Method D is indirect, whereby carbon dioxide present in the samples is first absorbed in alkali, subsequently acidified and the pressure of the evolved carbon dioxide measured manometrically. The apparatus used for this determination may be assembled from standard components of laboratory equipment and the total carbon dioxide content of the sample is obtained by relating the manometer readings to a calibration graph. Method E uses custom built commercial equipment and directly measures the pressure due to the carbon dioxide present. The free carbon dioxide content is determined by this method and is obtained by relating pressure gauge readings to tables supplied by the instrument manufacturers. Section F describes methods for the analysis of samples containing both sodium bicarbonate and carbon dioxide.

Part III gives details of sampling methods for sealed containers.

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 a series of booklets on single or related topics; thus allowing for the replacement or addition of the 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 and notes 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 technical staff 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 are 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 PITTEWELL
Secretary

1 July 1986

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 for one's self, one's colleagues, those outside the laboratory or work place, or subsequently for maintenance or waste disposal workers. 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. 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. Lone working, whether in the laboratory or field, should be discouraged.

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.

There are numerous handbooks on first aid and laboratory safety. Among such publications are: 'Guide to Safe Practices in 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.

It cannot be too strongly emphasized 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. If an ambulance is called or a hospital notified of an incoming patient give information on the type of injury, especially if poisoning is suspected, as the patient may be taken directly to a specialized hospital.



The Determination of Carbon Dioxide in Waters under Normal Atmospheric Pressure

Introduction

Natural waters obtained from sources within chalk or limestone geological formations, the so called "hard waters", contain a complex mixture of carbonic acid salts, whose stability and hence solubility, depend upon carbonate-bicarbonate equilibria maintained by the presence of carbonic acid — hydrated carbon dioxide species.

The equilibrium of such carbonate water systems is readily disturbed by changes in carbon dioxide concentration. A loss of carbon dioxide by heating, by exposure to atmosphere or by purging with inert gas, many result in insufficient carbon dioxide to sustain the bicarbonate ion solution equilibrium and insoluble calcium carbonate will be precipitated, as in either the familiar process of "scale formation" that occurs when hard waters are boiled or the stalactite, stalagmite formations found naturally in limestone areas. Carbon dioxide present in amounts in excess of that required to just maintain the presence of bicarbonate ions results in water that will dissolve chalk and limestone scale and the water is said to be "aggressive" or "corrosive". Thus the measurement of free carbon dioxide is an important parameter for the characterization of water.

Analytical techniques are available for the determination of free carbon dioxide such as gas stripping and titration with dilute sodium hydroxide solution.⁽⁵⁾ Gas stripping, using either an inert gas or carbon dioxide free air, is a precise method when applied to waters from which carbonic acid salts are absent e.g. naturally "soft" waters and waters subjected to "softening" treatments such as distillation or demineralization. However in the presence of substantial amounts of carbonic acid salts, shifts in equilibrium resulting from a loss of free carbon dioxide may result in the displacement of combined carbon dioxide and meaningful results may not be obtained.

Certain water treatment plants use air-stripping to remove excess carbon dioxide from naturally occurring carbonate waters. In this instance, an empirical air-stripping determination of carbon dioxide in which plant conditions are simulated in the laboratory may offer a satisfactory means of plant control. Hence, this possible application of gas stripping to carbonate waters is included in the gas stripping procedures of Section B of this part of the booklet.

Provided that the salts of other weak acids are absent and that the total salt concentration is less than ca 500 mg/l the laws of mass action relating to dilute aqueous solutions can be applied to carbonate water systems. Ionization constants for the dissociation of carbonic acid are accurately known and since the early years of this century many workers have derived theoretical equilibria. Notable among these have been the papers of Tillmans and Heublein⁽¹⁾, Larson and Buswell⁽²⁾, Dye⁽³⁾, and Langelier⁽⁴⁾ who have established relationships such as those between pH, hydroxyl, free carbon dioxide, bicarbonate, carbonate, temperature and solids contents. Langelier's work is especially noteworthy since he devised a formula from which a saturation value pH can be derived. A comparison between actual pH values and saturation pH value known as the "Langelier Index" determines whether or not a water is "aggressive" or that it is scale forming.

Such waters are not necessarily in equilibrium and a knowledge of the Index enables treatment by addition/removal of carbon dioxide to be effective in the establishment of an equilibrium. For instance an "aggressive" water is not suitable for supply in iron pipework and the carbon dioxide level should be decreased so that scale will be deposited to provide a protective carbonate coating and thus inhibit metal corrosion.

The sodium hydroxide titration method does not give a well defined end point owing to the slowness of the reaction between the titrant and free carbon dioxide^(5,6,7).

However only the basic concept of calculating free carbon dioxide is given in this booklet (see Section A1. Principle) and the references quoted above should be consulted if additional information is required.

Section C refers to a tentative ion selective electrode method in which an electrode of the gas-sensing membrane type may be used for the determination of either free or combined carbon dioxide. Continuing developments in electrode technology make it impossible to give a specific method.

A Calculation Method for the Determination of Free Carbon Dioxide

A1 Principle

The carbon dioxide content of the sample is calculated by inserting experimentally determined values of alkalinity and pH into a formula published by Larson and Buswell⁽²⁾ in 1942, reproduced by Dye⁽³⁾ in 1952 but based on much earlier work by Tillmans and Heublin⁽¹⁾ in 1912.

The formula is derived as given below:

The dissociation of carbonic acid is represented by the following equation:



The first dissociation constant of carbonic acid

$$k = \frac{[\text{H}^+] \times [\text{HCO}_3^-]}{[\text{CO}_2]} \quad (1)$$

$$\text{thus, } \log k = \log [\text{H}^+] + \log [\text{HCO}_3^-] - \log [\text{CO}_2] \quad (2)$$

$$\text{i.e. } -\log [\text{H}^+] = \log [\text{HCO}_3^-] - \log [\text{CO}_2] - \log k \quad (4)$$

$$\text{or } \text{pH} = \log [\text{HCO}_3^-] - \log [\text{CO}_2] - \log k \quad (5)$$

$$\log [\text{CO}_2] = \log [\text{HCO}_3^-] - \log k - \text{pH} \quad (6)$$

By expressing the molar concentration of bicarbonate ion as alkalinity, mg/1 CaCO₃, and the molar concentration of free carbon dioxide as mg/1 CO₂, the equation becomes:

$$\log \text{CO}_2 = \log \text{HCO}_3^- + \frac{\log 0.88}{k} - \text{pH} \quad (7)$$

This is "Tillmans' formula" for the calculation of free carbon dioxide. It relates the value of constant K at t°C (see Reference 8) to the values of pH and alkalinity determined at the same temperature t°C.

When the value of k at temperature t°C is substituted into Tillmans' formula

$$\log \text{CO}_2 = \log \text{HCO}_3^- + \log f - \text{pH}$$

Where f is a constant at t°C calculated from 0.88/k (Equation 7)

See also step A5.5 Note b.

The 0.88 term converts moles to mass.

A2 Interferences

Interference is caused by salts of weak acids other than carbonic acid⁽¹⁰⁾ which will contribute to the alkalinity, also humic acid which will contribute to the pH value of soft waters.

A3 Sample Collection and Preservation

Ideally the analytical procedure given in Section A5 should be carried out at the sampling site. However if this is impracticable fill a bottle (of about 1 litre capacity and preferably made of polyethylene) with sample so that no air remains inside the bottle. If glass containers are used these should be checked before use to ensure that the glass does not contribute to the alkalinity of the sample. (This may be done by storing a typical stable sample in the bottle and measuring the pH at intervals.)

Samples must not be agitated and should be analysed as soon as possible after collection since certain samples may undergo significant changes in storage.

There is no satisfactory method of preserving samples for the determination of pH and alkalinity and hence for the calculation of free carbon dioxide content.

A4 Apparatus

A4.1 pH Meter

A meter which is preferably portable and may be fitted with an automatic temperature compensation device.

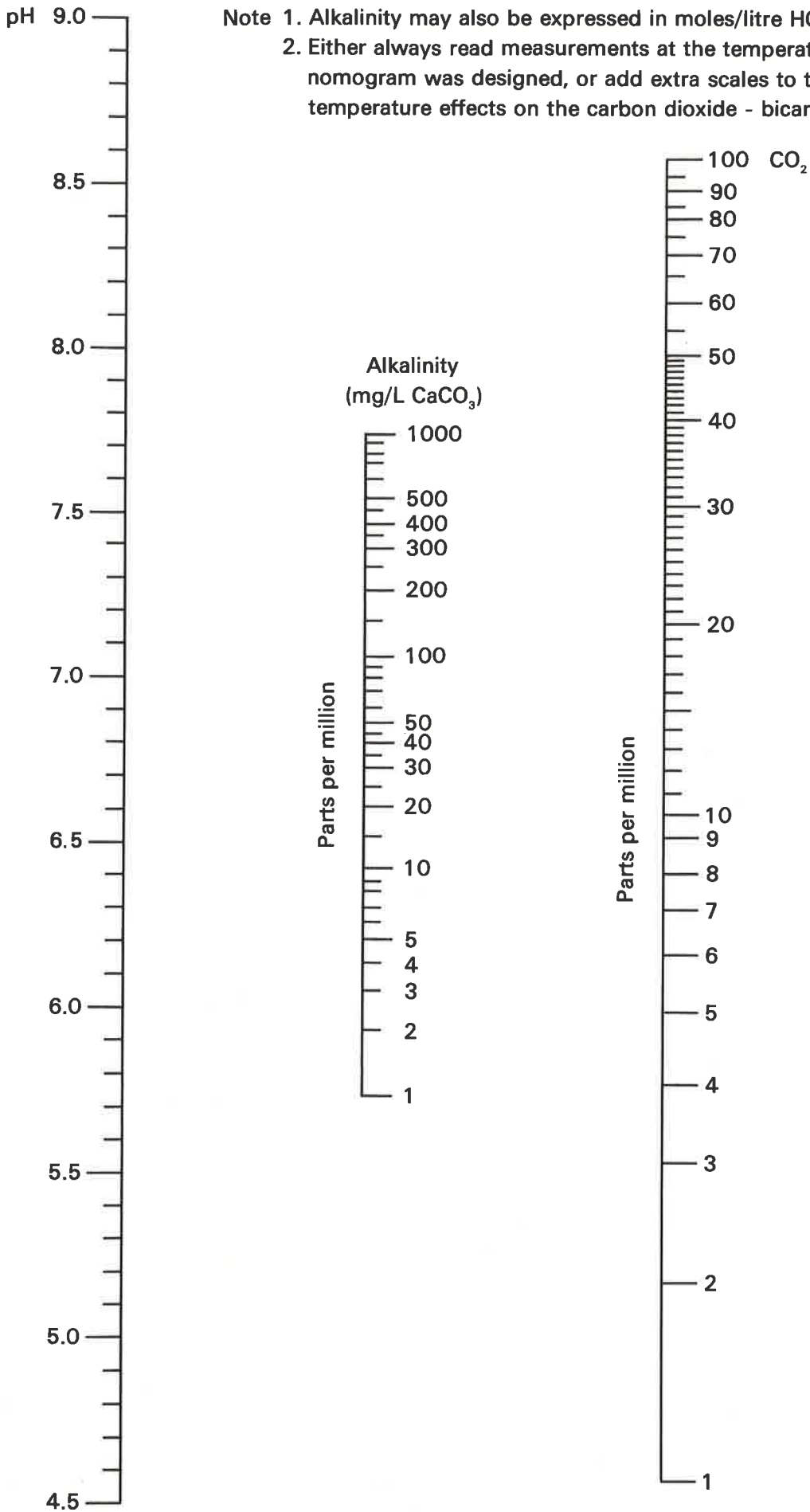
A4.2 pH Electrodes

Glass (measuring) and calomel (reference) electrodes compatible with the pH meter⁽⁹⁾.

A5 Analytical Procedure

Step	Procedure	Notes
A5.1	Measure the temperature of the water (t°C) (note a.) Without delay, carry out the remaining steps of this procedure.	a. Preferably all the steps given in this procedure should be carried out at the sampling point, where usually it will be possible to immerse a thermometer and pH electrodes directly into the water under test. Only for the alkalinity determination will it be necessary to transfer a suitable volume of the water to the flask for immediate titration with acid.
A5.2	With reference to Method B in the pH booklet in this series (9), set the pH meter in the manual temperature compensation mode at t°C and calibrate the meter with suitable buffer solutions at t°C.	However if it is not possible to carry out these determinations on-site, collect sample as given in Section A3 and <i>commence the analytical procedure with the minimum of delay such that all steps are carried out, as nearly as possible, simultaneously. Do not agitate the sample and measure the temperature, t°C at the same time that the pH measurement is made.</i>
A5.3	Measure the pH value of the sample (note a) in this manual temperature compensation mode. Let this value be P _t units. Alternatively set the pH meter in automatic temperature suitable buffer solutions. Measure the pH of the sample at t°C and let this be P _t units (note a.).	Prior to pH measurement, samples should not be allowed to warm up to laboratory temperature (if higher), or be held in a thermostatically controller bath at any chosen standard temperature above that of the sample when sampled, since changes in the composition, especially evolution or absorption of carbon dioxide, may occur. Allow sufficient time for the electrodes to attain equilibrium at the sample temperature, but avoid vigorous stirring which may change the composition of the sample.
A5.4	Determine the total alkalinity of the sample to pH 4.5 as given in Method A in another booklet in this series (10) and let this be A mg/l as CaCO ₃ (note a.).	

Figure 1 Typical nomogram relating pH, alkalinity and free carbon dioxide at one constant temperature (20°C)



- Note 1. Alkalinity may also be expressed in moles/litre HCO₃
- Note 2. Either always read measurements at the temperature for which the nomogram was designed, or add extra scales to take account of temperature effects on the carbon dioxide - bicarbonate equilibrium

A6 Calculation**A6.1**

Calculate the free carbon dioxide content of the sample (as mg/l CO₂) from the equation given below (note b):

$$\log B = \log A + \log f - P_t$$

Where A = total alkalinity of the sample (as mg/l)

P_t = pH value at t°C.

B = required free carbon dioxide content of the sample as mg/l CO₂

b. The following factors, which have been calculated as the mean values of the stated temperature ranges below may be used for the calculation of free carbon dioxide. If the tolerances given are acceptable, the exact values of k_t should be used in the equation above.

°C	f
5-9	0.277 × 10 ⁷ ± 5.1%
10-14	0.247 × 10 ⁷ ± 4.5%
15-19	0.224 × 10 ⁷ ± 3.6%
20-24	0.207 × 10 ⁷ ± 2.9%
25-29	0.194 × 10 ⁷ ± 2.6%
30-35	0.183 × 10 ⁷ ± 2.2%

The factor f, calculated from $f = \frac{0.88}{k_t}$ will be constant at any given temperature t°C (note b.). k_t is the dissociation constant at t°C, which may be calculated (8) from

$$-\log k_t = \frac{3404.71}{T} - 14.835 + 0.032786T$$

Where T is in degrees absolute (t+273)

A6.2

Alternatively construct a nomogram relating pH, alkalinity and free carbon dioxide content by substituting pH and alkalinity values determined at temperature t°C in the formula (A6.1) where k_t is the dissociation constant at the same temperature t°C.

e.g. at 20°C k_t = 4.140 × 10⁷ and f = 0.213 × 10⁷

A nomogram for 20°C calculated using this value of f is given in figure 1.

A6.3

For information on the construction of nomograms, see refs 21-23; for related examples see ref. 7. When using a computer it may be more convenient to express the formula within an appropriate programme into which values from steps A5.3 and A5.4 are inserted.

A6.4

Note that substituting for f in the equation in A6.1 simplifies as follows:

$$\begin{aligned} \log B &= \log A + \log f - P_t \\ &= \log A + \log \frac{0.88}{k_t} - P_t = \log A + \log 0.88 - \log k_t - P_t \\ &= \log A + \log 0.88 + \frac{3404.71}{273 + t} - 14.835 + 0.032786(273 + t) - P_t \\ &= \log A - 0.555 + \frac{3404.71}{273 + t} - 14.835 + 0.032786(273 + t) - P_t \\ &= \log A + \frac{3404.71}{273 + t} + 0.032786(273 + t) - P_t - 15.490. \end{aligned}$$

A7 Sources of Error

Errors that arise from the determination of alkalinity and pH value are quoted in the appropriate booklets of this series (9,10) and in the section on interferences (A2).

The sample must not be subjected to changes in temperature since changes in composition may occur and it is important that the value of the dissociation constant relates to the temperature at which the pH value is measured.

B**Determination of Air Strippable and Total Carbon Dioxide in Natural, Treated and Waster Waters****B1 Performance Characteristics of the Method****B1.1 Substances Determined**

Air strippable carbon dioxide and total carbon dioxide contained in the form of carbonates and hydrogen carbonates. In the absence of labile carbonic acid species gas strippable carbon dioxide represents free carbon dioxide.

B1.2 Type of Sample

Natural and treated waters (but see Section 3 Interferences).

B1.3 Basis of Method

Air stripping before and after acidification. The evolved carbon dioxide is absorbed into sodium hydroxide solution and the excess alkali is titrated with standard acid solution. (See also F3).

B1.4 Range of Application

0.5 to 50 mgm/litre of carbon dioxide as CO₂.

B1.5 Standard Deviation* (Total CO₂)

Nominal CO ₂ mg/litre CO ₂	Total standard deviation content	
	Lab 1	Lab 2
5	0.14	0.24
30	0.28	0.36

B1.6 Limit of Detection*

Lab 1 0.2 mg/1 CO₂ (13.d.f.)

Lab 2 0.6 mg/1 CO₂ (11.d.f.)

B1.7 Bias

Usually slightly negative but variable.

B1.8 Interferences

Sulphite ions may interfere. (See Section B3.)

B1.9 Time required for analysis

This is dependent on sample carbon dioxide content.

* Work carried out by two independent laboratories: London Transport Board, Lotts' Road Power Station, London and Imperial Chemicals Industries, Petrochemical Division, Wilton.

B2 Principle A large volume of sample (5 litres) is aspirated with carbon dioxide-free air before and/or after acidification. The evolved carbon dioxide is absorbed in an excess of sodium hydroxide solution, then titrated initially with hydrochloric acid solution to a phenolphthalein indicator end-point and finally to a pH value of 4.5 using bromocresol green/methyl red solution as indicator.

B3 Interference Hydroxide, phosphate and ammonia present in the original sample do not interfere. Sulphite ions, if present could produce acidic sulphur dioxide which would interfere. The interference can be minimized by the addition of sufficient potassium dichromate to oxidize the sulphite to sulphate.

If samples contain appreciable amounts of carbonic acid salts, e.g. naturally hard waters, the removal of carbon dioxide by gas stripping may disturb the equilibrium of the system resulting in an evolution of carbon dioxide in excess of free carbon dioxide. Transition metal bicarbonates and some carbonate complexes, especially of iron and manganese can also be decomposed. Consequently the results obtained from such samples should be interpreted with caution. However for the purpose of monitoring the performance of an air-stripping water treatment plant the method may give a meaningful result in terms of air-strippable carbon-dioxide.

B4 Hazards There are no special hazards associated with this determination other than those likely to be encountered in the preparation and handling of strong sulphuric acid and sodium hydroxide solutions.

B5 Reagents Reagents and chemicals of analytical grade quality shall be used. Water as prepared in Section 5.1 shall be used throughout this method.

B5.1 Water, carbon dioxide-free

Use de-mineralized or distilled water of pH not less than 6.0.

When distilling water for use in these methods add just sufficient sodium hydroxide to bring the water to pH 9 ± 0.5 , use a splash head above the flask and reject the initial 100 ml of distillate. Stop distillation before the pH in the boiler reaches 12 units.

If the pH of the water is less than 6.0 units, immediately before use boil the water for at least 15 minutes in a suitable flask and allow to cool to room temperature whilst keeping the flask closed with a guard tube containing soda-lime.

B5.2 Sulphuric acid solution (50% v/v)

Cautiously add 500 ± 5 ml of sulphuric acid (d_{20} 1.84) to 500 ± 5 ml of water with continuous stirring and cooling. Dilute the solution with water to $1,000 \pm 5$ ml and mix well.

Stored in a stoppered bottle this reagent is stable for at least 12 months.

B5.3 Standard hydrochloric acid solution (0.1N)

Using a graduated pipette fitted with a safety bulb add 9.0 ± 0.1 ml of hydrochloric acid (d_{20} 1.18) to a 1 litre calibrated flask. Dilute to volume with water and mix well. Standardize this solution as follows:

Weigh out accurately 0.1600 ± 0.0050 of sodium carbonate (B5.7) into a 250 ml conical flask and note the mass Mg of sodium carbonate taken. Add 100 ± 5 ml of water to the flask and swirl to dissolve the carbonate. Add 0.1 ± 0.02 ml of the pH 4.5 indicator solution (B5.5) and titrate with the hydrochloric acid solution to the disappearance of the greenish/blue colour. Note the titre T_1 ml. Carry out a blank determination using 100 ± 5 ml of water. Note the titre T_2 ml.

Calculate the normality (N) of the hydrochloric acid.

$$N = \frac{M \times 18.870}{(T_1 - T_2)}$$

Use the measured normality in further calculations or adjust to exactly 0.100N.

B5.4 Sodium hydroxide solution (c0.1M)

Dissolve 25 ± 0.5 g of sodium hydroxide pellets in 25 ± 0.5 ml of water with cooling in a 250 ml conical flask fitted with a cover. Allow to stand until the supernatant liquid is clear.

Using a safety pipette transfer 6.5 ml of the clear supernatant liquor to about 800 ml of water in a 1 litre calibrated flask. Dilute to volume with water and mix well.

Check the normality of the solution by titration against standard hydrochloric acid solution (B5.3) using indicator solution (B5.5). If necessary adjust the normality to within the range 0.95 to 1.005 by dilution with water or by the dropwise addition of clear supernatant concentrated sodium hydroxide liquor.

B5.5 Indicator solution (pH 4.5)

Dissolve 0.200 ± 0.005 g of bromocresol green (not water soluble grade) and 0.015 ± 0.002 g of methyl red (not water soluble grade) in 100 ± 2 ml of ethanol (95% industrial spirit). Store in an amber glass bottle.

B5.6 Phenolphthalein indicator solution

Dissolve 1 ± 0.1 g of phenolphthalein in 100 ± 2 ml of ethanol (95% industrial spirit) and dilute to 200 ± 4 ml with water. Mix well.

Alternatively, dissolve 1 ± 0.1 g of phenolphthalein in 120 ± 2 ml of 2-ethoxyethanol (Cellosolve) and dilute to 200 ± 4 ml with water. Mix well. Loss by evaporation is less with the latter solution and the dropping bottle does not become encrusted.

Immediately before use add sodium hydroxide solution (A5.4) dropwise to either of these solutions to the appearance of a faint permanent pink colour.

B5.7 Sodium carbonate (see B5.3)

Immediately before use dry 2 ± 1 g of sodium carbonate, anhydrous, for 60 ± 5 mins in an electric oven set at 265 ± 5 °C and allow to cool in a desiccator.

B5.8 Potassium dichromate (finely powdered)

B6 Apparatus

The apparatus shown in figure 2, required for this determination, is assembled from the following components:

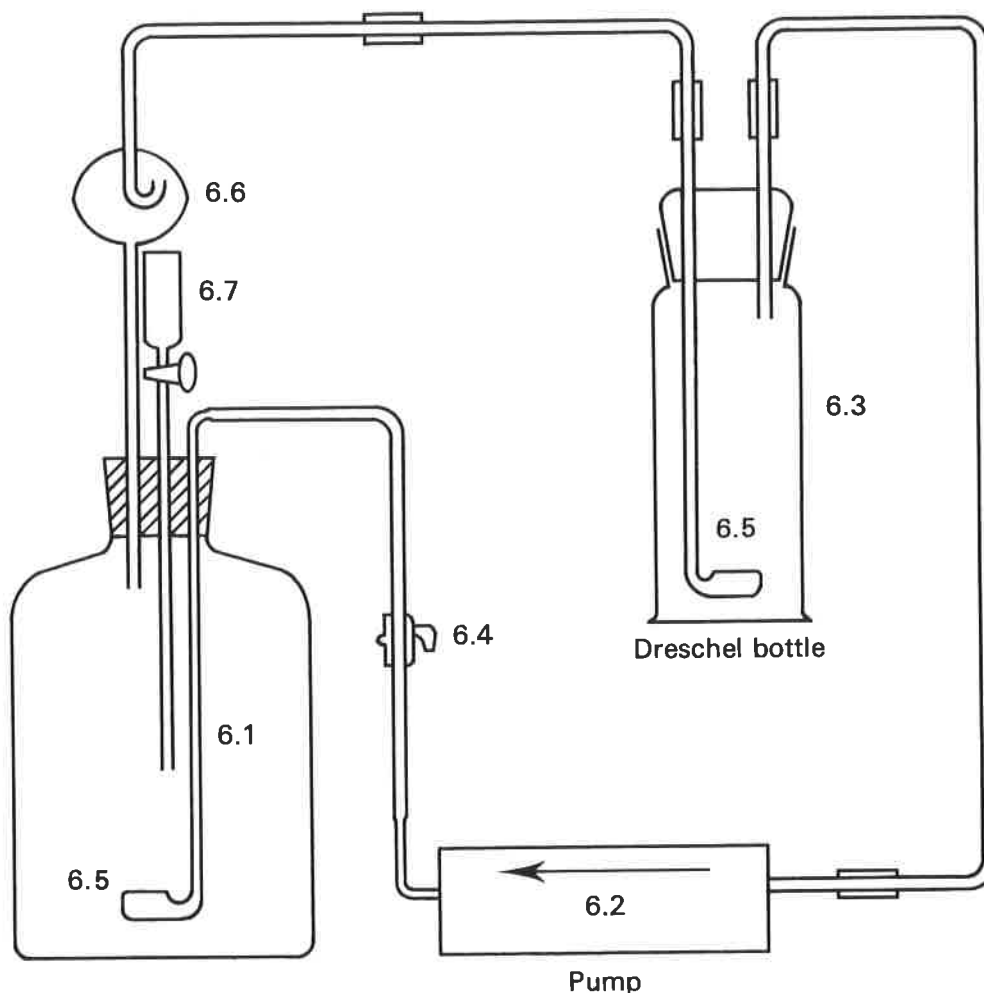
B6.1 Aspirator

This vessel shall be used to collect the sample; it may be either glass or polyethylene and of about 6 litres capacity; it shall be clearly marked with a 5 litre graduation; the free space above the graduation shall be between 500 ml and 1000 ml (see note below). A Buchner flask is also suitable.

Note: When analysing samples containing a low concentration of carbon dioxide, it may be necessary to correct for the carbon dioxide in the air in the free space. The correction is 0.1 mg/litre of carbon dioxide in the test sample for 1000 ml free space and a 5 litre test sample. (See also B8.14.)

B6.1.1 In addition to the stopper for sealing the bottle during transport and storage, a second stopper with three holes to carry items B6.5, B6.6 and B6.7.

Figure 2 Apparatus for the determination of carbon dioxide



B6.2 Diaphragm pump

A diaphragm type air compressor, capable of delivering 500 ml/minute of air against the head pressure inherent in the system.

B6.3 Dreschel bottle

A 250 ml Dreschel bottle, fitted with a sintered glass spoon (see B6.5).

B6.4 Screw clip

B6.5 Sintered glass spoons

Porosity grade 2 (British Standard 1752) (two) mounted on suitable lengths of glass delivery tubing to be fitted into aspirator (B6.1) and Dreschel bottle (B6.3).

B6.6 Splash head

(for B6.1).

B6.7 Tap funnel

At least 10 ml capacity (for B6.1).

B6.8 Calibrated glassware

10 ml, 20 ml bulb pipettes, 50 ml burette. All calibrated glassware used in this determination shall conform to the appropriate British Standards Specification and shall be thoroughly clean and grease-free.

B7 Sample Collection and Preservation

From a tap

Carefully collect 5 litres of sample in the aspirator from an appropriate sampling point, leading the sample to the bottom of the aspirator with a length of flexible tubing.

Avoid vortex formation or turbulence during sampling since this will result in the loss of free carbon dioxide.

From a body of water

When it is impractical to sample from a tap, transfer of the sample must be made in such a manner as to ensure minimal agitation.

Close the aspirator with a suitable gas tight stopper and carefully transport the sample to the laboratory for analysis.

Ideally the determination should be performed immediately, but where this is not practicable the sample is best stored at a temperature below that at which it was collected.

B8 Analytical Procedure

B8.0.1 Total Carbon Dioxide

If a determination of total carbon dioxide is required, carry out all the steps B8.1 to B8.13 in the procedure given below.

B8.0.2 Free Carbon Dioxide

If a determination of air strippable (free) carbon dioxide only is required then carry out steps B8.1 to B8.13 omitting step B8.5.

B8.0.3

Combined carbon dioxide may be obtained by subtracting the B8.0.2 value from the B8.0.1 value.

B8.0.4

Alternatively both air strippable and combined carbon dioxide may be determined individually on the same sample by carrying out the B8.0.2 procedure, followed by the B8.0.1 procedure with step B8.3 omitted.

B8.0.5 Removal of Interference

If the sample may contain sulphites or free sulphur dioxide add a small amount (c. 0.05 g) of finely powdered potassium dichromate to the sample and allow to dissolve and mix. If the yellow colour turns to a faint green or disappears add more potassium dichromate until further treatment produces no further reaction.

Step	Experimental Procedure	Notes
Determination of CO₂		
B8.1	Pipette a suitable accurately measured volume (note a.) of the 0.1N sodium hydroxide solution (B5.4) into the Dreschel bottle taking care to avoid excessive exposure to air. Dilute, if necessary to about 60 ml and add 0.5 + 0.1 ml of phenolphthalein indicator (B5.6).	a. the amount of sodium hydroxide solution required depends on the level of carbon dioxide expected and should be added as follows:

Step	Experimental Procedure	Notes	
B8.2	Re-connect the Dreschel bottle to the apparatus.	CO ₂ content mg/l	Vol. of 0.1N NaOH Solution ml
B8.3	Remove the stopper from the top of the sample aspirator and insert the bung carrying the splash head, sintered glass spoon and tap funnel. Connect the aspirator to the prepared apparatus ensuring that the bung is securely fitted and that the tap funnel is closed.	up to 10 10 to 20 20 to 30 30 to 50	20.0 30.0 50.0 60.0
B8.4	Check the assembly of the apparatus to ensure that all the joints are tight and that the screw clip is closed.		
B8.5	Acidify the sample by adding 10 ± 1 ml of sulphuric acid solution (B5.2) via the tap funnel (note b.). Ensure that the tap funnel is closed after the addition of acid.		b. If a determination of free CO ₂ is required omit the acidification of the sample and proceed to step B8.6.
B8.6	Switch on the diaphragm pump and adjust the screw clip to obtain as great a flow as possible without spray being carried over.		c. Suitable times for complete de-carbonation are from 1 hour for CO ₂ concentrations in the region of 20 mg/l to 2 hours in the region of 50 mg/l.
B8.7	Continue to circulate the air until the sample is completely de-carbonated (notes c. and d.).		d. If the phenolphthalein becomes colourless during the absorption stage abandon the determination and repeat using a larger volume of sodium hydroxide in the Dreschel bottle (see note a.) and a fresh sample.
B8.8	Test for complete de-carbonation of the sample by stopping the pump and replacing the Dreschel bottle containing the absorbed carbon dioxide with another containing water to which 0.5 ± 0.1 ml of phenolphthalein indicator solution (B5.6) and 0.1 ml of sodium hydroxide solution (B5.4) have been added. Restart the pump and circulate the air for a further 10 minutes; if the solution in the second Dreschel bottle remains pink, the sample has been completely de-carbonated (note e.).		e. If the phenolphthalein in this second sample becomes colourless, repeat the determination as in note d., but also increasing the circulation time.
Sample Titration			
B8.9	Dismantle the Dreschel bottle containing the absorbed carbon dioxide and rinse the sintered glass spoon and tube into the bottle with water (B5.1).		
B8.10	Titrate the solution in the bottle with standard 0.1N hydrochloric acid solution (B5.3) to a colourless end-point indicated by the phenolphthalein (pH 8.3). Note the titre T ₃ ml.		
B8.11	Add 0.1 ± 0.02 ml of pH 4.5 indicator (B5.5) to the Dreschel bottle and continue to titrate with hydrochloric acid solution (B5.3) to the disappearance of the greenish/blue colour (pH value 4.5). Note the total titre T ₄ ml.		

Step	Experimental Procedure	Notes
Blank Titration		
B8.12	Carry out a blank titration by repeating steps B8.1, B8.10 and B8.11 using the same volume of sodium hydroxide solutions (B5.4) as used for the sample. Note the titres T_5 and T_6 (ml) (note f.).	f. This is a blank on the sodium hydroxide used and not a true blank. A true blank is not only difficult to carry out but, if the determination is made with care, is unnecessary.
Calculation of Results		
B8.13	The concentration of carbon dioxide (CO_2 mg/litre) is calculated as follows:	
	$\text{CO}_2 \text{ (mg/l)} = [(T_4 - T_3) - (T_6 - T_5)] \times 8.8 \times N$	
	Where N is the calculated normality of the hydrochloric acid solution (B5.3).	
	$\text{Total CO}_2 = \text{Free CO}_2 + \text{Combined CO}_2 \text{ (See B8.0.1 to B8.0.4).}$	
B8.14	For low concentrations of carbon dioxide it may be necessary to correct for the air in the free space above the sample in the aspirator. (See also Note in Section B6.1.) A more exact correction for this free space carbon dioxide can be made by carrying out the whole procedure in an identical apparatus using as sample water which has been acidified to pH 3–4 and boiled briskly for at least ten minutes, cooled in a flask vented only through a tube containing fresh soda lime. This water must be measured, transferred to the sample aspirator with minimum contact with the air, and so obtaining an almost true blank. Errors will still arise if traces of carbon dioxide are picked up during this latter transfer and if the carbon dioxide content of the residual air differs greatly from that over the actual sample.	
B9	Extending the upper range of the method	The upper range of the method may be extended by taking a smaller sample volume in a correspondingly smaller size of aspirator e.g. a 3 litre aspirator would be suitable to handle 2.5 l of sample in order to give an upper limit of 100 mg/l CO_2 . The geometry of the apparatus may need to be revised in order to accommodate the modified aspirator. The calculation B8.13 would also need modification by an additional factor of $5/V$ where V is the volume in litres of the sample actually used.
B10	Sources of Error	These are normally associated with a possible loss of CO_2 during sample handling.

C

Note on Methods for the Determination of Free and Total Carbon Dioxide using an Ion-Selective Electrode

C1

No performance characteristics are quoted since they depend very much upon the model of electrode used and the mode of application recommended by the manufacturer.

C2

Principle

An electrode sensor of the gas permeable membrane type immersed in the sample responds to the partial pressure of carbon dioxide gas present (11, 12, 13, 14).

Carbon dioxide only, is able to permeate the hydrophobic polymer membrane, resulting in a change of pH in the sensor's internal filling solution, which is trapped around a glass pH electrode. The signal obtained from the glass electrode is related directly to the free carbon dioxide content of the sample.

When the probe is presented to the sample, as received, the sensor measures free carbon dioxide present at the equilibrium conditions prevailing within the sample at the time of measurement. If however the sample is acidified to pH 5 simultaneously with the introduction of the probe then total carbon dioxide is measured. Full details of electrode procedures may be obtained from the manufacturer of the electrode.

C3

Interferences

Hydrogen Sulphide, Sulphur Dioxide.

The Determination of Carbon Dioxide in Pressurized Bottled and Canned Waters

Introduction

These methods are applicable to sparkling effervescent waters in closed containers. The carbon dioxide content determined is that of the entire contents of the container and the analysis poses many problems, especially the minimization or prevention of the ready loss of carbon dioxide which can occur immediately the container seal is broken. Method D⁽¹⁵⁾ which is essentially a laboratory method minimizes the problem of carbon dioxide loss by cooling the sample.

Method E^(16,17) employs commercial pressure gauge apparatus fitted with devices adaptable to fit and pierce, various types of cans and the metal caps of glass bottles, without loss of carbon dioxide. This commercial apparatus does not necessarily require the use of a laboratory to carry out the determination and may in fact be readily portable for use in bottling plants. The method is only valid for samples preserved entirely with carbon dioxide.

These are followed by Section F, procedures for analysing mixtures of bicarbonate and carbon dioxide.

These methods are not suitable for the determination of very low levels of free carbon dioxide.

It must be emphasized that waters containing more carbon dioxide than is in equilibrium with one atmosphere pressure of carbon dioxide will rapidly lose carbon dioxide once that pressure is released. Furthermore, if the atmosphere above the sample, even if at the external atmospheric pressure, ceases to be entirely carbon dioxide (or changes if not originally pure carbon dioxide), then the sample will tend to equilibrate to that concentration which is in equilibrium with the partial pressure of carbon dioxide above it in the bottle. Hence as much preparation should be made as possible before opening the sample bottle and all subsequent work should be done as rapidly as possible without agitating the sample unnecessarily. Even so there is risk of some negative bias.

D

Indirect Method for the Determination of Carbon Dioxide in Bottled and Canned Mineral Waters

DI

Performance Characteristics of the Method

D1.1 Substance determined

Free and combined carbon dioxide

D1.2 Type of sample

Bottled and canned effervescent mineral waters.

D1.3 Basis of the method

The sample is treated with sodium hydroxide solution to absorb any free carbon dioxide present. This solution is then acidified to liberate carbon dioxide, the pressure of which is determined manometrically and related to the carbon dioxide content of the sample using a calibration curve.

D1.4 Range of application

0.5 to 6.0 g/l using 290 ml of sample.

D1.5 Standard Deviation

The batch within standard deviation of the method is approximately ± 0.2 g/l.

D1.6 Interferences

None.

D1.7 Time required for analysis

1½ hours, excluding the calibration procedure, which would require of the order of 1½ hours and may be carried out once each week.

D2

Principle

The sample in its original sealed container is cooled and treated with sodium hydroxide solution. The carbon dioxide present in this treated sample is evolved with excess acid and determined manometrically.

D3

Interferences

None.

D4

Hazards

D4.1 Concentrated acid and alkali solutions

The operator must wear safety spectacles and gloves when preparing and handling these reagents, which must not be pipetted by mouth.

D4.2 Mercury

Apparatus containing mercury must only be used in a well ventilated area and should be mounted within a tray to contain any mercury spillages, which should be immediately transferred to a sealed container.

D4.3 Apparatus under vacuum

All glassware must be thick walled and free from strains. When used under vacuum it must be shielded from the operator.

Note: Sample containers should be wrapped in thick towelling to minimize the effect of flying splinters in the event of breakage.

D4.4 Containers with samples treated with sodium hydroxide solution

Samples treated with alkali must be clearly labelled as unfit for consumption and must be thoroughly rinsed with tap water immediately after use.

D5 Reagents

Reagents and chemicals of analytical grade quality shall be used. Water as prepared in Section D5.1 shall be used throughout this method.

D5.1 Water, carbon dioxide free

Use de-mineralized or distilled water of pH not less than 6.0 units. (See Section B5.1). If the pH of the water is less than 6.0 units, immediately before use boil the water for at least 15 minutes in a suitable flask and allow to cool to room temperature whilst keeping the flask closed with a guard tube containing soda-lime.

D5.2 Sodium hydroxide solution (400 g/l)

Cautiously dissolve 200 g of sodium hydroxide pellets, with continuous swirling and cooling in about 350 ml of water in a loosely covered 1 litre conical flask. Dilute to 500 ml with water, and mix well. Store in a well stoppered polyethylene container.

Allow to stand before use to allow any sodium carbonate present to settle out.

In use remove the required volume of clear solution by pipette or syringe and minimize the exposure of the solution to atmospheric carbon dioxide. With care this solution is stable for at least 1 month.

D5.3 Sulphuric acid solution (50% v/v)

Cautiously add 100 ± 1 ml of sulphuric acid, d_{20} 1.84, to 100 ± 1 ml of water with continuous stirring and cooling in a 500 ml beaker. Dilute the solution with water to 200 ± 2 ml and mix well.

Stored in a stoppered bottle this reagent is stable for at least 12 months.

D5.4 Sodium carbonate anhydrous

Dry about 20 g of sodium carbonate, anhydrous, for 60 ± 5 minutes in an electric oven at $265 \pm 5^\circ\text{C}$. Allow to cool in a desiccator.

D5.5 Standard sodium carbonate solutions

Weigh out accurately to within ± 0.0002 g the separate amounts of sodium carbonate anhydrous (D5.4) shown in the table below. Dissolve in about 90 ml of water. Make up to 100 ± 1 ml with water. Add by safety pipette 5 ± 1 ml of 400 g/l sodium hydroxide solution (D5.2) and mix well. Store in a stoppered container.

Mass of sodium carbonate anhydrous (g)	Equivalent to Carbon Dioxide (g/l)
0.4817	2.0
0.7225	3.0
0.9633	4.0
1.2042	5.0
1.445	6.0

Note: These standard solutions are prepared on the basis that a mineral water would require the addition of 5 ml of 400 g/l sodium hydroxide solution per 100 ml of sample.

D5.6 Silicon grease

High vacuum grade

D6 Apparatus

D6.1 Reaction flask

A 100 ml B19 conical flask, fitted with a central well, 8 mm internal diameter, 25 mm deep as shown in Figure 3.

D6.2 Vacuum tap two way

D6.3 Vacuum tap three way

D6.4 Mercury trap

D6.5 Manometer

Mercury filled, of the dimensions shown in Figure 3. The apparatus is assembled as shown in Figure 3 and preferably used inside a laboratory maintained at a constant temperature to within $\pm 2^\circ\text{C}$.

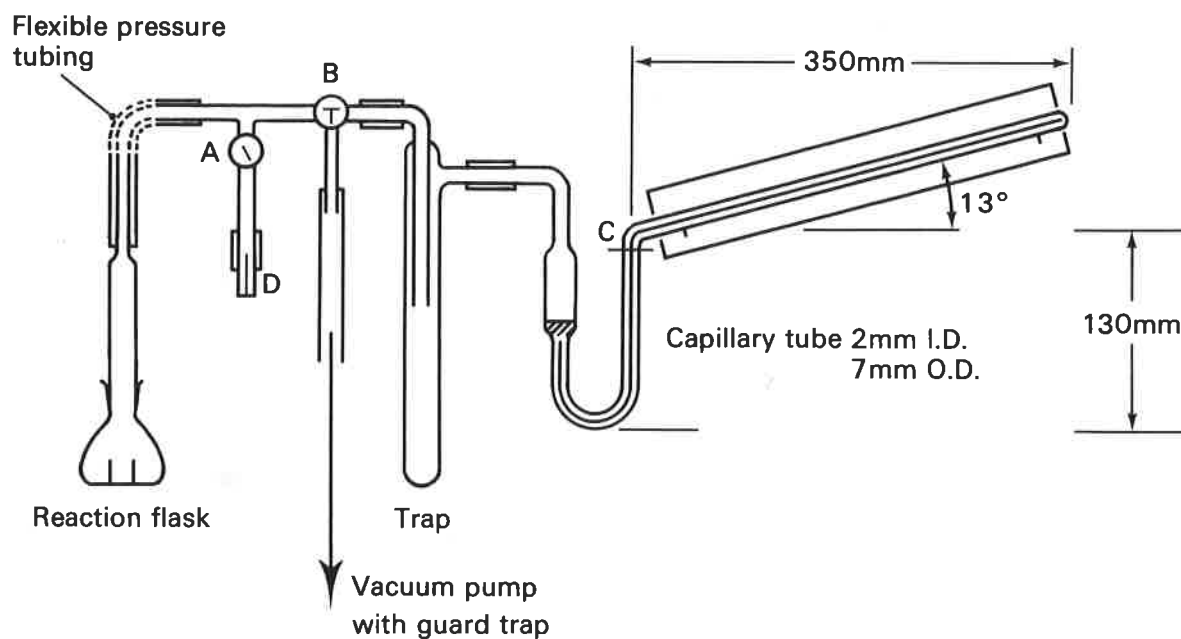
D6.6 Vacuum pump

Capable of operating at a reduced pressure of 1 mm.

D6.7 Safety pipettes

0.5 ml, 5.0 ml and 10.0 ml.

Figure 3 Diagram of apparatus for manometric estimation of carbon dioxide



A Two-way vacuum top

C Zero setting

B Three-way vacuum top

D Drawn-out capillary air bleed

D6.8 Refrigerator

Capable of cooling sampling container and contents to 0 °C.

D7 Sampling and sample preparation (See also Part III.)

D7.1 Sampling

The sample will usually take the form of an individual nominal half-pint sealed glass bottle or metal can. If the container represents a sample obtained from a batch of containers the analyst must ensure that it has been selected in accordance with statistical principles.

D7.2 Sample preparation

(See also Part III Section 3.4.)

Cool the sample container to 0 ± 0.5 °C for at least 1 hour, but do not freeze. If the sample is thought to contain a significant proportion of carbonic acid salts see Section F before proceeding. Carefully remove the bottle stopper (e.g. crown or screw cap) or pierce the metal can and add sodium hydroxide solution (400 g/l) in the proportion of 5.0 ± 1 ml per 100 ml of sample. Mix well, but avoid introducing air into the solution and use with the minimum of delay in the procedure given below in Section D8.

D8 Analytical Procedure

Step	Procedure	Notes
Determination of Total Carbon Dioxide		
D8.1	Pipette 5.0 ± 0.05 ml of sample into the outer compartment of the reaction flask (note a.).	a. If the expected carbon dioxide content of the sample exceeds 6.0 g/l a reduced sample volume must be taken and calculation (D8.14) amended.
D8.2	Using a safety pipette add 0.5 ± 0.1 ml of sulphuric acid solution (D5.3) to the central well of the reaction flask.	See also Section F2.
D8.3	Lightly grease the ground joint of the flask and connect to the apparatus at point A (note b.).	b. Sample determinations and the calibration procedure, steps D8.11 to D8.14 should be carried out at the same temperature.
D8.4	Close the two way tap B.	
D8.5	Position the three way tap C so that the reaction flask and manometer are connected to the vacuum source.	
D8.6	Allow the mercury level in the manometer to fall below the zero setting point.	
D8.7	Turn tap C so that only the flask is connected to the manometer.	
D8.8	Using tap B adjust the manometer mercury level to the zero point.	
D8.9	Mix the contents of the flask by tilting and shaking it vigorously (note c.) until the mercury level in the manometer reaches a constant level. Note this reading and let it be H mm.	c. Hold the flask lightly by the neck only.

Step	Experimental Procedure	Notes
Calibration Procedure		
D8.10	Pipette 5.0 ± 0.05 ml of a standard sodium carbonate solution into the outer compartment of the reaction flask.	
D8.11	Proceed as given above for the sample in steps D8.2 to D8.9 and let the manometer reading obtained be L_1 mm.	
D8.12	Repeat the calibration procedure steps D8.10 and D8.11 using each of the remaining standard sodium carbonate solutions in turn. Let the manometer readings obtained be L_2 , L_3 , L_4 and L_5 mm respectively.	
D8.13	Plot the manometer readings $L_1 \dots L_5$ against the corresponding carbon dioxide content (g/l) of the standard solution and draw in the line of "best fit" to obtain the required calibration curve.	
D8.14	Calculation Relate the manometer reading H mm obtained for the sample to a calibration curve prepared as given in steps D8.10 to 13 to obtain the total carbon dioxide content of the sample (note d.).	d. The calibration graph relates to a sample volume of 5.0 ml. If a different volume has been used an appropriate correction is necessary.

D9 Sources of Error

D9.1 Carbon dioxide present in reagent solutions.

D9.2 The introduction or loss of carbon dioxide during processing of the sample.

E

Direct method for the Determination of Carbon Dioxide in Bottled and Canned Waters using commercial apparatus

- E1 Performance Characteristics of the Method**
- E1.1 Substance determined
Absorbed carbon dioxide.
-
- E1.2 Type of sample
Bottled and canned mineral waters, in which carbon dioxide occurs naturally, or to which carbon dioxide has been added.
-
- E1.3 Basis of the method
Measurement of the pressure due to carbon dioxide absorbed in the sample and the relation of this to the carbon dioxide content of the sample by use of tables.
-
- E1.4 Range of application
2 to 12 g/l carbon dioxide.
-
- E1.5 Precision
Dependent upon the commercial apparatus used.
-
- E1.6 Interferences
Other gases than CO₂ soluble at the bottling pressure.
-
- E1.7 Time required for analysis
Approximately 5 mins per reading.
-
- E2 Principle**
The sample container is pierced by a probe carrying a pressure gauge. After the release of head space pressure and when equilibrium at known temperature has been attained, the gauge reading is related to the carbon dioxide content of the sample using tables.
- E3 Interferences**
In principle see E1.6; but in practice none have been reported.
- E4 Hazards**
The usual laboratory hazards and those associated with the handling of pressurized containers, especially glass bottles. The apparatus and sample containers should be provided with a screen to protect the operator and the container should also be wrapped in thick towelling to minimize the effect of flying splinters in the event of breakage.
- E5 Apparatus**
- E5.1 Carbonation Tester
Such as:
“Universal Carbonation Tester”, suitable for all sizes of bottles and cans irrespective of the type of closure.
Screw clamp type for use with “crown capped” glass bottles.
Clamp-on tester specifically for use with metal cans.

Rotary tester in which a sample bottle is placed inside a cylinder. The cap is pierced by a device carrying a pressure gauge and the cylinder is rotated manually to agitate the sample to ensure that maximum pressure is recorded by the gauge.

The only known manufacturer of the apparatus listed above is W. Reeve and Co. Ltd, Merton, London, SW19 3UU.

E5.2 Thermometer 0–50 °C.

E6 Sampling and sample preservation

Obtain samples in the form of glass bottles or metal containers. If the determination cannot be carried out immediately upon receipt, the sample should be stored in a cool place away from direct sunlight.

See also Part III.

E7 Analytical Procedure

Step	Procedure	Notes
E7.1	Bring the sample in its container to 15°C ± 3°C (note a.).	a. Avoid shaking the bottle.
E7.2	Attach the sample container to the testing apparatus (E5.1) as given in the manufacturer's instructions (note b.).	b. Ensure that a gas tight seal is obtained.
E7.3	Pierce the closure or top and withdraw piercer.	
E7.4	If there is appreciable free space between the closure or top and the liquid, open the snift valve, slowly and carefully, without disturbing the apparatus (note c.) and observe the pressure gauge reading. When the pressure gauge reading has fallen to zero close the valve. If the top space is minimal proceed directly to step E7.5	c. It is essential to carry out step 4 extremely carefully to minimize the possible loss of carbon dioxide from the sample. In glass bottles such loss can be seen as a stream of bubbles rising to the surface of the liquid.
E7.5	Shake, rotate or agitate the apparatus until a constant pressure reading is obtained on the gauge. Note this reading.	
E7.6	Detach the sample container from the apparatus and open. Insert a thermometer and note the sample temperature.	
Calculation		
E7.7	Relate pressure A units and temperature T °C to tables provided by the instrument manufacturer to obtain the carbon dioxide content of the sample.	

E8 Standardization If tables are not available calibration curves can be prepared by carbonizing appropriate water samples to different pressures of carbon dioxide. Prepare several samples at each pressure. Divide each pressure batch into three, analyse one set by this method and use the other two for determination by Method F assuming that a soluble bicarbonate is present. Prepare a calibration curve from this data.

E9 Sources of Error

The sample containers contain a significant volume of air since air is used as a counter pressure at filling plants. The initial "snifting" step E7.5 will minimize interferences from air but at the same time carbon dioxide may be lost from the system (see Part II Introduction). If an analysis of the air or inert gas is required see Section G3.5.

F

Analysis of samples containing Free Carbon Dioxide and Sodium Bicarbonate

F1 Introduction

Unless it is necessary to know the bicarbonate ion content separately for purposes of making an ionic balance on a natural water, for waters containing 6 g/l or more of total carbon dioxide with an alkalinity corresponding to less than 6 millimoles HCO_3^- (600 mg/l as CaCO_3), equivalent to at most 250 mg/l carbon dioxide, a separate analysis is unnecessary as the bicarbonate fraction is comparable with the experimental errors. However, for samples with 3 g/l or less of total carbon dioxide and similar alkalinity, separate analyses may be useful.

F2 Analytical Procedure

F2.1

Transfer a suitable aliquot of sample to a pre-ignited and tared reaction flask, evaporate to dryness and weigh. If the dissolved solids are not negligible ignite the flask and residue for 1 hour at 400°C. Cool and determine carbon dioxide as given in Section D8. Let the carbon dioxide found be B g/l.

F2.2

Determine the carbon dioxide content of the second aliquot of sample treated with alkali as given in Section D7. Let this be A mg/l.

If A falls between B and 2B: no free carbon dioxide is present i.e. only carbonic acid salts are present.

If $A > 2B$: free carbon dioxide is present.

$$\text{Free carbon dioxide} = A - 2B \text{ g/l.}$$

F3 Alternative Analytical Procedure

Although the manometric measurement of evolved carbon dioxide is well established⁽¹⁸⁾ greater precision may possibly be obtained by sweeping the evolved carbon dioxide with nitrogen into a tared soda-lime tube via a desiccant guard tube and thus determining the mass of carbon dioxide collected by subsequent reweighing. The tared soda-lime tube should have integral inlet and exit taps to guard against pick up when not in use. The desiccant used must not absorb carbon dioxide. An extra exit side desiccant/absorbant guard tube is advisable in many laboratories.

Part III

G

The Sampling Methods for Waters in Bottles, Cans, Containers and Syphons

G1 Introduction Because some but not all bottled waters are carbonated, and some may be under pressure with gases other than carbon dioxide, the sampling procedure used is dependent on:

1. the purpose of the analysis;
2. whether under gas pressure or not;
3. the type of container.

G2 Sampling of tanks or containers used for bulk storage on trains, aircraft, buses and ships These samples should normally be taken at the tap with the same procedure as used for domestic consumers' tap samples. Sampling frequency should take into account the risk of contamination when filling and venting and the volume and storage life of the water in the tank. Samples should also be taken on a statistical basis when tanks are filled routinely. If for any reason it is necessary to take a dip sample great care is needed in precleaning the cover area to ensure that no contamination falls into the water during sampling. Similar care is necessary if prior mixing is essential.

G3.1 Selection of bottles etc. from a batch or stock

Bottles etc. should be selected at approximately equal intervals through a production run or stock in store, the total number selected having regard to the volume of the container and the total volume of water to be sampled.

G3.2

Except when sampling for free carbon dioxide and pressurizing gases, bottles or containers should be well mixed by turning end over end for 15 minutes prior to analysis. Bottles for free carbon dioxide and gas analysis should not be shaken at all.

G3 Sampling of Water in sealed bottles, containers or syphons

G3.3

For any analysis except for free carbon dioxide, pressured containers may have their pressure released slowly. However, for syphons it may be more convenient to use the syphon pressure to expel the requisite sample volume into a clean glass or plastic bottle or flask (depending on determinand) and stopper this container after gas evolution has ceased. Bottles, after release of any pressure, should be treated as sample bottles for ordinary tap water analysis, samples being taken carefully to avoid any contamination, and bottles reclosed immediately.

G3.4 For determination of free carbon dioxide and inert pressurizing gases

In addition to carbon dioxide, samples usually contain natural or added carbonate salts. For a complete analysis, at least 3 measurements are necessary requiring at least 2 separate samples. The measurements are:

- a. Total gas pressure (see Method E above);
- b. Total carbon dioxide plus carbonates;
- c. Combined carbonates.

Sections G3.4.2 to G3.4.4 are each subdivided accordingly.

Measurements (a) and (c) can often be made on the same sample which may subsequently also be usable for sampling as in paragraph G3.3 above.

Determination (b) requires a separate sample which should be taken from a bottle or container as close in production order to the bottle used for determinations (a) and (c) as possible.

G3.4.1 The sampling procedures for these 3 determinations vary with bottle or container type. There are 3 variants:

- i. bottles and cans with thin metal, cork or plastic stoppers penetrable by a hypodermic needle;
- ii. bottles and syphons etc. under pressure and fitted with valves;
- iii. contains with glass balls, hard plastic or porcelain stoppers.

These are discussed in turn below.

G3.4.2 For containers penetrable by a hypodermic needle:

a. For gas pressure

Fix or clamp a rubber pad over the cap or top and insert a small volume stiff metal capillary tube with a point at one end, fitted with a pressure measuring device at the other. There must be no gas leakage until the measurement is completed. After measurement of total gas pressure, provided no contamination has occurred, this sample may be vented to remove dissolved gases and used for other tests except total carbon dioxide. Because of risk of contamination this sample is not recommended for use for bacteriological examination.

b. For total carbon dioxide and carbonate

With a fresh bottle or container fit a rubber pad as in (a), then using a similar stiff metal capillary tube and a syringe or piston pipette inject a known volume of accurately known strength sodium hydroxide solution into the sample, sufficient to convert all free carbon dioxide to bicarbonate. Set aside a similar portion of the same solution in a stoppered container for use as a reagent blank.

Rinse out the syringe or pipette by sucking sample up into it and reinjecting several times.

As the volume that can be injected may be very small, this hydroxide solution may need to be strong.

Allow the sample and excess sodium hydroxide to mix thoroughly, then vent the can or bottle and proceed as for tap water samples. (Note absence of excess pressure after sodium hydroxide addition indicates absence of inert pressurizing gas.) Prior to analysis, measure the volume of the sample plus alkali and thus obtain the sample volume.

c. For Combined Carbonates

Vent the sample and proceed as for water samples G3.3.

G3.4.3 Bottles and syphons etc. fitted with valves (if procedure G3.4.2 is not possible)

a. For gas pressure

Fix the pressure measuring device to the valve outlet by as short a length of suitable pressure tubing as possible. Slowly open the valve. Reclose the valve at the end of the test.

b. For total Carbon Dioxide and Carbonate
(use a fresh bottle)

Fit the valve outlet with a delivery tube dipping to the bottom of a tall jar, cylinder, or a beaker containing an excess known volume of preanalysed sodium hydroxide solution. The container should be large enough to hold the whole contents of the sample. Very slowly, controlling by the valve, transfer the whole contents of the sample to the vessel containing the sodium hydroxide, ensuring that all free carbon

dioxide reacts. Rinse off the dip tube with a known amount of water. Prior to analysis measure the volume of the sample plus alkali and rinse water and thus obtain the sample volume. Mix well and store the sample in a clean stoppered glass bottle until needed.

c. For combined carbonate
As in Section G3.3 above.

G3.4.4 Containers with glass balls, hard plastic or porcelain stoppers

a. Gas Pressure measurements are not readily made with these types of container, but collection of gas samples is possible, see Section G3.5, free carbon dioxide being determined by difference between (b) and (c) below.

b. For total carbon dioxide and carbonate
Take a clean beaker large enough to contain at least twice the contents of the container to be sampled. To this beaker add a known volume of known strength sodium hydroxide solution and if necessary a sufficient known volume of water to ensure that when inverted in the beaker the top of the bottle to be sampled is several centimetres below the liquid surface. Thoroughly clean the bottle and its cap, without loosening the cap. Clean a pair of tongs. Invert the bottle and immerse the cap in the liquid in the beaker. Then by means of the tongs loosen the bottle cap or stopper and slowly let sample and gas flow into the beaker. Mix thoroughly, remove the bottle, stopper and tongs allowing them to drain thoroughly into the beaker. Measure the sample volume and store the sample in a clean stoppered bottle until needed.

c. For combined carbonate.
Transfer the contents of the bottle to a clean stoppered bottle, allow gases to vent, before stoppering tightly.

G3.5 Analysis of gases present not soluble in sodium hydroxide

Take a glass sampling cylinder, of sufficient volume to hold all the gas expected to be evolved from the sample, fitted with a single tap vent at one end and 2 tap vents at the other. Fill the whole cylinder including vent nipples with water, close all 3 taps, suspend over a tank of water large enough to contain the container to be sampled with the double valve end dipping under the water (be careful not to get air into the nipples). Immerse a funnel in the water in the tank, connect one of the two adjacent cylinder vents to the funnel. Place the container to be sampled into the water and arrange the cylinder and funnel over the top of the immersed container with both the adjacent vents still immersed, open both these vent taps. Then slowly open the container allowing gas to escape slowly into the funnel and so into the gas sampling cylinder. When no more gas is given off, close the 2 taps on the cylinder and assemble the cylinder into a gas dispensing device or gas analyser using one tap at each end. For more accurate results, measure the volume of the water used in the procedure and determine any carbon dioxide that may have dissolved during the gas collection.

Analytical Quality Control

Analysts are usually advised to keep a control sample, analyse it at regular intervals and plot a control chart (19, 20). While this can be done for pH measurement and alkalinity, it is impossible to reuse a free carbon dioxide sample. It is suggested that a series of sealed samples be prepared, either all saturated at constant conditions, or containing known weights of added carbon dioxide.

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