RIVER POLLUTION

I. CHEMICAL ANALYSIS

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PREFACE

FOLLOWING the appearance of my book 'Aspects of River Pollution', it was suggested in some quarters that Chapters 9 and 10 of that book, reviewing methods of detecting and determining the various forms of pollution and discussing the interpretation of the results, might well form the theme of a separate publication. The present volume represents, therefore, a revised version of those chapters which it is hoped will appeal to all interested in chemical analysis as applied to river pollution problems, sewage and trade wastes. The importance of analysis in helping to safeguard the purity of our rivers can hardly be overstressed.

Since the larger work was written, two important practical handbooks on the analysis of effluents have appeared in this country. First, late in 1956, H.M. Stationery Office issued the Ministry's 'Methods of Chemical Analysis as applied to sewage and sewage effluents', a thorough revision of the original edition of 1929. Secondly, in 1958, there appeared for the first time in this country 'Recommended Methods for the analysis of trade effluents' prepared by a Joint Committee of the Association of British Chemical Manufacturers and the Society for Analytical Chemistry; these methods have also been published individually in 'The Analyst' from January 1956 to April 1958. Advantage has been taken during the preparation of this book of incorporating the recommendations of these two publications.

A bibliography of nearly 600 references has been appended, of which no less than 87 cover work published during 1957 and 1958, but many more would be needed for a complete literature survey. In this connection, it may be apt to point out that the 'Bibliography on water and sewage analysis' by B. H. Weil, P. E. Murray, G. W. Reid and R. S. Ingols, published in 1948 as Special Report No. 28, State Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia, U.S.A., contains 2560 references. This useful and invaluable indexed guide carries the literature up to the end of 1947 but even then does not include every paper on water and effluent analysis. Other first-rate sources of analytical methods are the 'Analyst', the American 'Analytical Chemistry', the excellent 'Water Pollution Abstracts' published monthly for the Water Pollution Research Laboratory by H.M. Stationery Office, 'Chemical Abstracts' issued by the American Chemical Society, and

'Analytical Abstracts' published since 1954 by the Society for Analytical Chemistry.

My thanks are due to Dr. B. A. Southgate, C.B.E., Director of the Water Pollution Research Laboratory, for allowing me to reproduce a table showing the solubility of oxygen in water based on work carried out by that laboratory. A similar table for sea-water from a paper by G. A. Truesdale and A. L. H. Gameson has been reproduced by courtesy of the Secretary General of the Bureau du Conseil International pour l'Exploration de la Mer in whose Journal it was published.

I am also greatly indebted to Mrs S. M. Rawson, B.Sc., Assistant Chemist, Mersey River Board, for reading and criticising the manuscript.

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ABBREVIATIONS

ABCM—SAC Joint Committee.   Association of British Chemical Manufacturers and Society for Analytical Chemistry Joint Committee for the analysis of trade effluents

A.P.H.A.   American Public Health Association

B.D.H.   British Drug Houses

B.O.D.   Biochemical Oxygen Demand

EDTA   Ethylene diamine tetra-acetic acid (sodium salt)

M   Molar, i.e. a solution containing the molecular weight in grams of a substance per litre of solution

N   Normal, i.e. a solution containing 1 gram equivalent of substance, or amount of substance equivalent to 1·008 grams of hydrogen, per litre of solution

p.p.m.   parts per million (i.e. grams per million millilitres,* or milligrams per litre)

‰   parts per thousand (grams per kilogram)

<   less than

>   greater than

mg/l.   milligrams per litre

h   hours

ml   millilitres

gr   grains

μg   micrograms (i.e. millionths of a gram)

The abbreviations appearing in the Bibliography are taken from *World List of Scientific Periodicals* (Butterworths, London)

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* Definition given by Ministry of Housing and Local Government in Circular No. 8/54, 1954. In British units, it is for all practical purposes approximately equal to lb. per million lb. or lb. per 100,000 gal.

CHAPTER 1
INTRODUCTION

MUCH pollution of the rivers of this country by sewage and trade wastes has been going on since the days of the Industrial Revolution over 150 years ago. The Rivers Pollution Prevention Act, 1876, did something to improve the position, especially because it led to the formation of River Authorities in certain industrial areas (e.g. the Mersey and Irwell Joint Committee, the Ribble Joint Committee and the West Riding of Yorkshire Rivers Board). Since the Second World War, there has been a renewed interest in pollution problems owing to the expansion of industry, the growing scarcity of sources of water, and the ever-increasing usage of water for domestic and industrial purposes. Evidently new legislation was needed to replace the existing law so that better control over pollution could be exercised. The establishment by the River Boards Act, 1948, of River Boards covering all the watersheds of England and Wales and dealing with land drainage, fisheries, and pollution prevention was an important step in this direction. This was followed by the passing of the Rivers (Prevention of Pollution) Act, 1951, which gave up-to-date legal powers to these new Boards. A similar Act for Scotland, the Rivers (Prevention of Pollution) (Scotland) Act, 1951, set up and also provided legislation for Scottish River Authorities which were termed 'River Purification Boards' since, unlike the English Boards, they dealt with pollution prevention only.

It is obvious that since most pollutions are of a chemical or physical nature, chemical analysis supplemented by physical and physico-chemical procedures must play a vital part in the detection and measurement of river pollution. Many excellent handbooks giving practical details of analytical methods suitable for water, sewage, trade wastes and river waters have appeared in recent years (see references 1–25) and it is not the purpose of this book to encroach upon the ground covered by these publications. Rather is it the intention to provide a chemical background for, and supplement to, the information on analytical methods and in addition to review critically other methods which, though not officially recommended, may nevertheless be useful in certain circumstances for research, control work and field tests.

Before commencing analytical work it is essential to have a clear idea about the purpose of the analysis. It may be conducted

for research purposes or for the control and management of a sewage disposal works or of trade premises. The determination of the strength of a sewage or trade waste may be needed to gain an idea of the capacity of the various treatment units and, for trade wastes discharging to sewers, to decide what pre-treatment is required. It may be vital to determine impurities likely to affect adversely sewers, men working in sewers, or the treatment and disposal of sewage. It may be necessary to assess the effect of discharges upon a river, to determine whether these discharges satisfy certain standards and to carry out river surveys for these purposes.

River surveys are carried out for a number of reasons. The surveys may be merely of a routine character conducted to obtain an idea of the quality of the stream water at various points and under varying weather conditions, and if possible to assess the effect of the many pollutions. In this way, valuable data can be obtained providing a basis for a comparison of the state of the stream at different seasons and in different years. Surveys may also be undertaken for research purposes, or with the intention of formulating by-laws or taking legal proceedings under the Rivers (Prevention of Pollution) Act, 1951, or with the object of investigating some complaint such as mortality amongst fish, odour nuisance, or unsuitability of the river water for industrial and other uses. Whatever the purpose in view, the detection and identification of the particular pollution or pollutions followed by the application of quantitative methods to determine the extent of the pollution must constitute a fundamental feature of the survey. For this purpose, various procedures are available making use of hydrological, physical, chemical, bacteriological and biological techniques. In this book only the chemical and physical methods are discussed.

It is rarely necessary to undertake an elaborate survey using all the methods and techniques reviewed here, and often a simple field survey utilizing a limited number of tests and methods suffices. The choice and number of methods used will depend to a large extent upon the purposes in view, on the nature of the problems encountered, on the staff and funds available, on the periods of time over which observations are taken, and on local circumstances. In making a choice amongst a number of available procedures for a particular constituent, such factors as accuracy, the time taken to perform the test, the limitations of the method, the interferences likely to be encountered, and the concentration of the desired constituent must all be considered.

The sampling for a physical and chemical examination of discharges of sewage effluents and trade effluents and of stream waters forms an important feature of a river survey (see references 26–35A). Samples should be taken in clean, colourless glass bottles provided

with ground-in glass stoppers; half-Winchester bottles holding one quart (or about 1 l.) are convenient for this purpose but the amount of sample required may be more or less than this quantity depending upon the nature and composition of the sample and upon the completeness of the analysis. Certain determinations (e.g. dissolved oxygen, oil, sulphide) must be performed on a separate sample taken specially for the purpose in another bottle. It is a wise precaution when sampling to rinse the bottle once or twice with the sample. Care should be taken to see that a representative sample containing the true proportion of suspended matter to liquid is obtained and it is obvious that any deposit on the bottom of the stream, sewage fungus growing on the bed, etc., should not normally be included (such extraneous matter should be separately collected and examined).

The taking of a sample in a bottle of absolutely clear and colourless glass facilitates a general description of the appearance of the sample. The description of the settled sample should include the smell, the colour, and the degree of turbidity of the supernatant liquid as well as the colour, apparent quantity and general characteristics of the sediment (e.g. whether finely divided, flocculent, sandy, etc.). The sediment, which may include dead and living material, frequently has a characteristic appearance under the microscope, consequently a microscopic examination should rarely be omitted. Dead material may be chiefly of mineral origin (e.g. sand granules from the river bed or from a sand washery) or it may be predominantly organic (e.g. coal-dust, cotton fibres, wool, paper pulp, starch granules). Living material can include algae, filamentous organisms (e.g. 'sewage fungus'), yeast cells (from brewery wastes), protozoa, crustacea, etc., and the identification of these by biological methods frequently yields valuable information. Sewage sludges, if present, may contain dead as well as living material.

The observations of WEBBER[26] are of particular relevance in connection with sampling:

'The actual collection of the water sample is a matter of considerable importance, more especially as this is often done by laymen with little knowledge of such matters. There can be few responsible chemists who have not received a grubby bottle filled with dirty water late on a Friday afternoon, accompanied by a vague note dated the previous Saturday. On opening the "sample", it may reek to high heaven of cough mixture, "Evening in Paris", or gin. Such efforts are completely useless.'

The label on the sample bottle should include such information as the type of sample (e.g. stream water, sewage effluent, trade effluent, etc.), the source (e.g. name of stream, firm, or local authority),

the exact position of the sampling point (an Ordnance map reference may be necessary), the date, the time, the temperature of the sample, the weather and particulars of recent weather conditions, the visible state of the river (e.g. whether above or below normal flow, whether in spate), the state of the tide if the river is tidal, whether taken in the middle, left or right bank, and at what depth, and any other relevant data which might assist the analyst. The signature of the person taking the sample should also appear on the label and if possible the name of the person in whose presence the sample is taken, and the label should bear a reference number.

If a bacteriological analysis is required, a special sample should be taken under aseptic conditions in a sterilized glass bottle (capacity about 200–250 ml.) provided with a ground-in dust-proof stopper; if a river water is being sampled, the stopper is removed below the stream surface and against the flow. Precautions to be observed and other recommendations in connection with sampling for bacteriological tests are given in a Ministry of Health report[5].

River samples are often taken at a point halfway between the surface and the bed of the stream, carefully avoiding the disturbance of sediment at the bottom.   Since, however, the mean velocity of a stream on any vertical is usually found at approximately $0.6 \, h$ from the surface (where h = depth) it has been suggested that sampling should be done at that depth.   Much depends upon local circumstances and it may be necessary in some cases (especially near effluent outfalls) to take samples at different depths.   For a fuller discussion of the precautions to be taken when sampling and of the most suitable sampling positions, the reader is referred to the literature (see especially references 1, 2, 3, 6, 7, 14 and 27). When it is necessary to take river, sewage and trade samples at frequent intervals during the day, the use of automatic sampling devices is often desirable[29, 31-33], and is particularly useful at large sewage works receiving discharges of trade wastes[33].   Samples should be kept in a refrigerator at about 4° C if the analysis cannot be carried out immediately, since it has been shown in the case of sewage and sewage effluents[34] that considerable changes in composition may take place on storage at ordinary temperatures owing to biochemical action.

Section 15 of the River Boards Act, 1948, specifies that where it is desired to use an analysis of a sample as evidence in legal proceedings, the occupier of the land or the local authority must be notified of the fact that an analysis is to be carried out.   The person taking the sample must divide the sample into three parts each of which must be placed in a bottle or container and sealed.   One part is handed to the occupier of the land or the local authority, another part is kept for court inspection, and the third part is analysed.

When a river board wishes to make an application to the Minister under the Rivers (Prevention of Pollution) Act, 1951, for consent to take proceedings in respect of pollution of a stream by sewage effluent or trade effluent the stream water should be sampled, according to a Ministry circular[35A], both above and below the alleged source of pollution, and, if at all possible, a sample of the effluent itself should be taken.*

HANEY and SCHMIDT[35A] have pointed out that many forms or indications of pollution are not readily susceptible to precise quantitative determination but nevertheless may sometimes figure prominently in legal actions involving river pollution.   Examples are odours, froth, scum, oil, discoloration, floating masses of putrefying sludge, objectionable solids or slimes on the stream bed, and dead fish.   In many of these instances photography can be a useful and intelligible aid as a record of pollution and far more persuasive than masses of figures.   The position is well put by these authors:

> 'One carefully composed well-documented photograph, particularly if it is in colour, may be worth a hundred dissolved oxygen samples in so far as securing public support or influencing a jury is concerned.'

It may not be amiss to add a few words on the question of the accuracy of the methods used in the chemical examination of samples.   The degree of accuracy normally attainable in chemical work of this kind is of the order ±5 per cent and this is sufficient for most routine work.   For research work, a higher degree of accuracy is desirable and for this purpose lengthy proceedures are often necessary involving the use of expensive apparatus and equipment and careful attention to detail.   For most routine work and field tests, time is a most important consideration and it is desirable to use quick straightforward methods.   There is a tendency in some of the newer methods of today to use complex procedures and expensive equipment where a simpler and more direct approach might be sufficient for the purpose.   A modern method is not always better than an older well-tried one; indeed, the word 'modern' is often applied to justify something that has little other merit.   It must be remembered, too, that the accuracy of a method is limited by the accuracy of the sampling which is generally not of a very high order.   The position is well summarized by LOVETT and FISH[18]:

> 'Frequently, extreme accuracy is not essential in routine testing, and providing the limitations of a particular procedure are fully

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* It may not be feasible to get a sample of the effluent if the outlet is submerged or if the discharge takes place in a culvert.

appreciated, it may be a great advantage to make some sacrifice regarding accuracy, particularly if appreciable saving in time results therefrom.'

It is important, however, to emphasize that this does *not* mean that slipshod work is condoned or that it matters little if an end-point be overstepped by several drops of titrant.   In general, then, it is better to be prudent and use a simple straightforward method whose errors and limitations are known rather than a so-called 'improved' procedure of doubtful soundness. Let us, therefore, adopt towards these newer but insufficiently tested methods a somewhat cautious attitude of mind.

Needless to say, arithmetical calculations involved in analytical and survey work should be carefully checked either by means of a slide rule, or by the use of books of mathematical tables[41-44]. Although the metric system of weights and measures is used wherever possible and chemical results are now generally expressed in parts per million (p.p.m.)*, i.e. grams per million millilitres, or milligrams per litre, large scale data are frequently determined in the imperial system and conversion from the one system to the other is often required.   A few common conversion factors are given in the Appendix but a more complete list is to be found in a publication of the British Standards Institution[37] and in handbooks of chemical and physical constants[38-40].

In the analysis of sea water[287, 288], results for chlorinity, salinity and the major constituents are generally expressed in parts per 1000 (grams per kilogram of sea water).   Another unit, however, is coming into use in the literature, especially for the minor constituents, viz milligram-atoms or microgram-atoms per litre of sea water at 20° C.

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* In the U.S.A., the latest edition of the A.P.H.A. *Standard Methods*[2] recommends the use of the more precise term 'mg. per litre' (instead of p.p.m.) and this is also recommended by the ABCM—SAC Joint Committee

PHYSICAL METHODS

A DISCUSSION of physico-chemical methods with full details of their practical application to all kinds of problems is given in the standard works by REILLY and RAE[45], and GIBB[46], to which the reader is referred for further information.

TEMPERATURE

It is usually sufficiently accurate to take the temperature of a stream water or an effluent to the nearest half degree centigrade. For more accurate work, especially in connection with the calculation of the percentage saturation of dissolved oxygen, a standardized thermometer graduated in tenths of a degree centigrade should be used.

COLOUR AND TURBIDITY

The purest natural river waters are generally colourless and the presence of any colour at all is usually an indication of the presence of organic matter, which may impart a straw, yellow or brownish tint to the water. It is possible in these cases to express the colour in terms of the Hazen standard unit, i.e. the colour given by 1 p.p.m. of platinum in the form of chloroplatinic acid modified by the addition of 2 p.p.m. of cobaltous chloride hexahydrate[2, 4]. This determination is much simplified by using the B.D.H. Lovibond nesslerizer and a disc with nine permanent glass standards ranging from 5 to 70 Hazen units[139, 140]. If much suspended matter is present, the estimation of colour should be made after settlement or centrifuging.

With many polluted waters containing highly coloured wastes (e.g. textile dye wastes), the colour may be green, blue, purple, black, etc., and so cannot be determined by the simple procedure just outlined. In such cases, use can be made of the Lovibond tintometer in which the colour is matched by a suitable combination of graded red, yellow, and blue glass filters and expressed in terms of the internationally used Lovibond units.

RUDOLFS and HANLON[47, 48] have described accurate spectrophotometric and filterphotometric methods of determining colour in waters and industrial wastes in terms of the dominant wavelength (which defines the hue or kind of colour), luminance (which defines

the degree of brightness) and purity (which defines saturation, i.e. pastel, pale, etc.).   The procedure is given in the latest edition of the A.P.H.A. *Standard Methods*[2].   For most purposes, however, it is sufficient to express the colour of a river water or trade waste in purely qualitative terms.

PALIN[49] has proposed a standard definition of colour in water in terms of optical density.   The Unit* ('Absorptiometric Colour Unit') is that of a clear water having an optical density of 0·001 per cm depth to violet light (peak wavelength 425 mμ, i.e. the wavelength at which the yellow-brown colour of most natural waters shows a maximum absorbance).   When a water is both coloured and turbid, the colour reading must be corrected for the influence of turbidity (see p. 9).   Various commercial turbidimeters, visual and photoelectric, are available for the measurement of turbidity and they are generally calibrated against standards made up from fuller's earth, a correction being made for any colour in the sample[14]. In the U.S.A., the unit of turbidity was, until recently, the turbidity imparted to a water by 1 p.p.m. of fuller's earth.   This unit has now been abandoned in favour of arbitrary turbidity units fixed in relation to a standard Jackson candle turbidimeter[2].   This change has evidently been made because, as experience in this country also shows, standards prepared from fuller's earth vary somewhat with the source and grade of material used and so do not give reproducible results.

A submersible photoelectric absorptiometer specially suitable for the measurement of high turbidities in river waters was used in the survey of the Thames estuary by SCRAGG, BRIGGS and KNOWLES[50]. To obtain the calibration curve, the instrument was placed in water free from turbidity (i.e. water of 100 per cent transmission) and by the use of various neutral density filters, dial readings were obtained corresponding to a particular optical density or percentage transmission.   Curves showing the relation between the optical density and various types of suspended matter of differing nature and particle size were also constructed.

The use of the Zeiss–Pulfrich nephelometer for determining the turbidity of river waters has been described by RIES[51].

For rapid routine work, an inexpensive visual apparatus [1, 3, 52] for measuring approximately the clarity or transparency of a·sample (which is inversely related to its degree of turbidity) can be constructed from a colourless glass tube, 620 mm long, and of internal diameter about 25 mm with a plane glass bottom on the outside of which a black cross (with lines 1 mm in width) is pasted.   A side tube near the bottom connects, via rubber tubing, with a glass reservoir, and the depth of liquid in the tube is adjusted by raising

* This Unit is 2·5 times the Hazen unit.

or lowering the reservoir until on looking down the tube, preferably in north daylight, the black cross just disappears from sight. The length of the liquid column in millimetres is measured or read off from graduations on the tube. If the test is performed on the settled as well as shaken sample, the difference gives a good idea of the amount of suspended matter present. With good effluents or river waters, the black cross may still be visible even at a depth of 600 mm, in which case the result is recorded as >600 mm. Most satisiactory sewage effluents and good trade effluents give settled transparency figures of 300 mm or more. Poorly clarified sewage or trade effluents may give readings of less than 100 mm.

Palin[49] has proposed a new Absorptiometric Unit of turbidity which is that of a suspension having an optical density of 0·001 per cm depth to yellow light (peak wavelength 580 mμ)*. Turbidity and colour can thus be determined photometrically using two different light filters. Colour can be corrected for turbidity and vice versa by determining the values of the ratio

$$\frac{\text{Optical density to violet light}}{\text{Optical density to yellow light}}$$

at the two wavelengths for both colour and turbidity. Palin found that this ratio is 4·7 for natural colour in water and 1·2 for turbidity (using relatively coarse fuller's earth suspensions).

pH VALUE[53-57]

Wide-range and narrow-range test-papers for the approximate estimation of pH values ranging from 2·0 to 10·5 are available commercially.† These papers are convenient for rough work and for field tests. The use of the British Drug Houses universal indicator is also convenient for obtaining an approximate idea of the pH value of a sample, the colour obtained at various pH values being indicated in *Table 1*.

Table 1. Colours obtained at various pH values with B.D.H. universal indicator

pH value	Colour	pH value	Colour
3·0	Red	8·0	Green
4·0	Deeper red	8·5	Bluish–green
5·0	Orange–red	9·0	Greenish–blue
5·5	Orange	9·5	Blue
6·0	Orange–yellow	10·0	Violet
6·5	Yellow	10·5	Reddish–violet
7·0–7·5	Greenish–yellow	11·0	Deeper reddish–violet

* This Unit is almost identical with the arbitrary APHA turbidity unit[2]. For practical purposes, the difference is negligible.

† For instance from the British Drug Houses, Poole, Dorset; and from Johnsons, Hendon, London, N.W.4.

More accurate determinations of pH (usually to within 0·1 pH unit over the range 0·2–10·0) can be made with the Lovibond comparator* in which, with the aid of a series of suitable discs, the colour obtained with 10 ml. of sample plus an appropriate amount of a suitable indicator (usually 0·5 ml.) is matched against Lovibond permanent glass colour standards. With many pure river waters and other samples which are poorly buffered (e.g. samples having a methyl orange alkalinity, expressed as $CaCO_3$, of less than about 20 p.p.m.), an appreciable error can be introduced due to the pH value exerted by the indicator itself. In such cases, it is preferable to use the B.D.H. Lovibond nesslerizer in which 50 ml. Nessler tubes replace the 10 ml. tubes of the comparator and a much smaller

Table 2. *Selected list of indicators suitable for the colorimetric determination of* pH *in the range* 0·2–14·0 *with the Lovibond comparator or the B.D.H. Lovibond nesslerizer*

Indicator	pH range of colour disc (in steps of 0·2 unless otherwise indicated)	Instrument C=Comparator N=Nesslerizer		Colour change acid→alkaline
Cresol red (acid range)	0·2–1·8	C		red—orange—yellow
Thymol blue (acid range)	1·2–2·8	C	N	purple–red—orange—yellow
Bromophenol blue	2·8–4·4	C	N	yellow—purplish–grey—purple–blue
B.D.H. '3046' indicator	3·0–4·6	C	N	purple—grey—green
Bromocresol green	3·6–5·2	C	N	yellow—green—blue
B.D.H. '4460' indicator	4·4–6·0	C	N	red—orange—yellow—green
Bromocresol purple	5·2–6·8	C	N	yellow—grey–purple—violet
Bromothymol blue	6·0–7·6	C	N	yellow—green—blue
Cresol red (alkaline range)	7·2–8·8	C	N	yellow—orange—pink—violet-red
Thymol blue (alkaline range)	8·0–9·6	C	N	yellow—greenish—blue
B.D.H. '8610' indicator	8·6–10·0	C		yellow—orange—pink—red
B.D.H. '9011' indicator†	9·0–11·0	C	N	yellow—grey—violet-grey
B.D.H. '1014' indicator‡	11·0–14·0	C	N	green—brownish–grey—pink—orange

     † 5 standards in steps of 0·5.
     ‡ 9 standards in steps of 0·5.   Unsuitable in presence of lime.

* Obtainable from Tintometer Ltd., Salisbury, or from the British Drug Houses, Poole, Dorset.

proportion of indicator solution (0·2 ml.) is taken.   With this instrument, the colour is matched looking vertically down the column of liquid and not, as in the case of the comparator, horizontally through the liquid.   Some useful indicators suitable for use with these two instruments are given in *Table 2.*

The colorimetric determination of pH can also be carried out accurately by comparing the colour produced by the sample plus a specified amount of indicator with that of buffer solutions of known pH containing the same amount of indicator.   Lists of suitable indicators are given by SNELL[53], BRITTON[55] and TOMICEK[58].

When samples are coloured or very turbid, and generally when greater accuracy is required, the electrometric method utilizing the glass electrode is to be preferred.   The calibration of the glass electrode is carried out using buffer solutions whose pH value is known with a high degree of accuracy.   *Table 3* gives the pH values of aqueous solutions of standards that have been recommended for this purpose.

Table 3.   Calibration of glass electrode for pH *determinations:* pH *values of standard solutions at various temperatures* (° C)

Standard substance	Formula	Composition of solution M=Molar	pH					Reference
			14°	15°	20°	25°	26°	
Potassium tetroxalate	$KH_3(C_2O_4)_2 \cdot 2H_2O$	0·1 M	—	—	—	1·48	—	56, 59
Potassium tetroxalate	$KH_3(C_2O_4)_2 \cdot 2H_2O$	0·01 M	—	—	—	2·15	—	61
Potassium bitartrate	$KHC_4H_4O_6$	Saturated	3·55	—	—	3·56	—	60, 61
Potassium hydrogen phthalate	$C_6H_4\overset{/COOH}{\underset{\backslash COOK}{}}$	0·05 M	4·000	4·000	4·001	4·005	—	56
Borax . . .	$Na_2B_4O_7 \cdot 10H_2O$	Saturated	9·40	—	—	—	9·34	60
Borax . . .	$Na_2B_4O_7 \cdot 10H_2O$	0·05 M	—	—	9·18	—	—	62
Lithium carbonate .	Li_2CO_3	Saturated	11·51	—	—	—	11·36	60
Trisodium phosphate	Na_3PO_4	0·01 M	—	—	—	11·72	—	61
Calcium hydroxide	$Ca(OH)_2$*	Saturated	—	—	—	12·45	—	63

* Prepared from CaO obtained by igniting pure $CaCO_3$.   Recommended by the U.S. National Bureau of Standards for measurements in the strongly alkaline range.

OIL AND OTHER IMMISCIBLE LIQUIDS

According to KIRSCHMAN and POMEROY[64], oil is the 'relatively nonvolatile liquid component that contributes to the formation of oil films and deposits'.   This definition excludes oils that evaporate rapidly at ordinary temperatures; such oils are usually of minor importance in river pollution, since owing to their volatility, they do not often contribute to the formation of oily films on the surface of a stream.   In the normal procedures for determining oil based on extraction with a volatile solvent and evaporation of the extract, volatile oils would, of course, not be included since they would be lost by volatilization.   There may be instances (e.g. discharges to sewers) when relatively volatile oils may be of some importance and

an ingenious method for their determination has been described by SHERRATT[65, 66]. The method involves removal of the volatile oil by a current of air, adsorption of the oil on activated carbon and extraction with acetone; dilution of the acetone extract with acid Teepol gives a turbidity which can be compared with a series of standards containing petrol or other suitable volatile oil.

Oil is usually determined by extracting the acidified sample with a suitable organic solvent (e.g. light petroleum, hexane, ethyl ether, or chloroform), removing the solvent from the extract by evaporation or distillation, drying the residual oil at 100–105° C, and weighing. The method is only approximate since it gives not only oil but also fat, tar, and any grease associated with the suspended solids. Kirschman and Pomeroy[64] describe a wet extraction procedure for determining oil in oilfield waste waters using commercial hexane as solvent; the latter was removed by distillation on the water-bath and the oil obtained was finally dried at room temperature. More reproducible but slightly lower results were obtained by these authors by a flocculation method using zinc acetate and sodium carbonate, the precipitated zinc carbonate trapping the oil very effectively; after filtering and air-drying the precipitate, the adsorbed oil was extracted with hexane. Small amounts of oil can be estimated by flocculation with iron salts[67]. Ferric chloride is added to the sample which is then heated to boiling and precipitated with ammonia. The precipitated ferric hydroxide, which entrains all the oil, is filtered, washed with water and dried, and the oil is then extracted from the precipitate with ether.

A flocculation method, using magnesium sulphate and lime (or other suitable flocculents), followed by acidification of the precipitate and extraction with light petroleum is recommended by the ABCM-SAC Joint Committee[66].

A sub-committee of the American Petroleum Institute[67A] examined several methods for determining oil in refinery effluents and concluded that the best was a procedure involving extraction of the oil with CCl_4 and measurement of the infra-red absorption at $3·42 \mu$ and $3·50 \mu$. Almost as good, and using much cheaper equipment, was an extraction-pycnometer procedure in which the density of the CCl_4 extract was compared with that of the pure solvent.

PRINGLE[68] has described a method suitable for very small quantities (up to 10 p.p.m.) of oil. The sample ($2\frac{1}{2}$ litres) acidified with hydrochloric acid is shaken with benzene and to prevent emulsion formation hydrogen is generated by introducing magnesium wire. The benzene layer is distilled and the residual oil is dried at 100° C.

POMEROY[69] has devised a useful test for the estimation of the floatable oil and grease present in waste waters discharging to sewers.

The estimation of very slight traces of oil is difficult by ordinary

methods but HOLLAENDER[70] has determined as little as 0·02 p.p.m. of oil in steam condensate by comparing the fluorescence under ultra-violet light with that of standards.

Oil often consists of motor fuel oil or lubricating oil derived from petroleum. Such oils dissolve in light petroleum giving a brown solution exhibiting a greenish fluorescence. Standard methods for testing such oils are given in a recent publication[71]; important characteristics of these oils are specific gravity, distillation range, flash point, viscosity, and behaviour on heating and ignition. If coal-tar oils are present, they should show the special reactions for phenols and will give a strong phenolic odour on ignition. The Standardisation of Tar Products Tests Committee have published standard methods for testing tar and its products[72].

A special sectional sampling tube has been recommended for the taking of representative oil-water samples[52].

ELECTRICAL CONDUCTIVITY[2, 7, 45, 73]

GUSTAFSON and BEHRMAN[74] have recommended the determination of electrical conductivity as a rapid means of checking results of the determination of total dissolved solids as obtained by the evaporation method which is often slow and not always very accurate owing to losses of certain mineral constituents. It may be necessary to dilute the sample first and it is essential to remove any free carbon dioxide by aeration with air free from carbon dioxide.

Although the determination of electrical conductivity is useful in the analysis of potable waters in showing changes in the concentration of total ionizable salts, its application to river survey work is somewhat limited. Nevertheless, it can be used to indicate alterations in the content of ionizable salts in river waters due to such discharges as brine, oil-field waste waters, and chemical wastes. A convenient commercial instrument (the dionic water tester*) is available for this purpose and this can easily be checked from time to time against a standard solution of potassium chloride.

An instrument has been described for measuring the salinity of estuaries by a conductivity determination with an accuracy of + 0·33 parts per 1000 over the range 0·2–50 parts per 1000; the temperature and electrical conductivity having been determined, the salinity is estimated from a nomogram[75].

The unit used for expressing conductivity is the reciprocal of 1 megohm per centimetre-cube. Results should be corrected to a standard temperature (generally 20° or 25° C). Conductivity increases very markedly with rise in temperature, usually approximately 2 per cent per degree centigrade.

* Made by Messrs. Evershed and Vignoles, London.

MACKERETH[76] has made use of determinations of electrical conductivity for measuring the cation concentration (Ca, Mg, Na and K) and the anions of strong and weak acids in diluted river waters after the latter have been passed through columns of strongly basic and acidic ion exchange resins.

SUSPENDED SOLIDS, SETTLEABLE SOLIDS, DISSOLVED SOLIDS AND TOTAL SOLIDS[1-3, 14, 16, 77-87]

Two standard methods are in use in this country for the determination of suspended solids.

The Gooch crucible method involves the filtration by suction of a known volume of the shaken sample through a specially prepared asbestos mat in a Gooch crucible, which is then dried at 100–105° C. The preparation of a series of such crucibles for routine work is rather laborious and filtration is sometimes very slow particularly with polluted samples containing much colloidal matter and greasy suspended matter. Moreover, it is difficult to prepare a standard mat and the suspended solids figure obtained will depend to some extent upon the thickness of this mat. Studies of the method by DEGEN and NUSSBERGER[77] showed that to reduce errors to a minimum the following points were important:

(1) the crucible should have *small* perforations,
(2) soluble salts should be washed from the filter mat after filtration,
(3) the asbestos should be of good quality,
(4) filtration should be carried out at a lower vacuum than that used in the preparation of the mat, and
(5) loss of fine asbestos particles should be avoided during filtration and washing.

Several workers have reported favourably on the use of a glass fibre filter disc in place of an asbestos mat in the Gooch crucible method[77A, 77B].

In the alternative centrifuge method, which the writer prefers, a known volume of the shaken sample (usually 50–200 ml.) is centrifuged under standardized conditions using special conical-end centrifuge tubes. After pouring off the separated liquid, the suspended matter at the bottom of the tubes is washed with distilled water, re-centrifuged, the separated water is again removed, and the suspended matter is transferred to a weighed platinum or other suitable basin by means of a jet of water from a wash bottle and dried at 100–105° C. In general, this method is much quicker than the Gooch crucible method, especially when large numbers of samples are being examined, but gives slightly lower results as it does not include any colloidal matter that tends to be retained by

the Gooch mat. Indeed, the work of RUDOLFS and BALMAT[78] has definitely shown that the so-called 'suspended solids' determination as carried out by the filtration of raw sewage through a Gooch crucible does include a portion of the colloidal fraction. Another advantage of the centrifuge method lies in the ease with which a determination of volatile solids can be subsequently carried out by ignition of the platinum basin containing the suspended solids; during this ignition, valuable information about the nature of the suspended solids can be obtained by noting any blackening, darkening or colour changes, any odours produced, evolution of fumes, appearance of sparks, flame, etc. The mineral residue remaining after ignition should be subjected to a qualitative analysis for the commoner cations and anions, especially calcium, magnesium, iron, chromium, copper, zinc, lead, sulphate, chloride and phosphate.

The filtrate from the Gooch crucible, or the separated liquid in the centrifuge, can be used for a determination of 'dissolved solids' or 'soluble solids' by evaporating a known volume to dryness. Any colloidal matter present will also be included in this determination.

FRASCHINA[81] prefers to estimate suspended solids in sewage by filtration through a weighed filter paper on a Buchner funnel, and considers that this method is quicker and easier for plant control than the Gooch crucible method. Correction is made for moisture absorbed by the filter paper during weighing.

A rapid photoelectric method for suspended solids estimation suitable for the control of sewage plant operations is described by SETTER and his co-workers[82] and involves the measurement of the percentage light transmission of the sample after homogenization for 30 sec in a Waring Blendor. The suspended solids can then be estimated from calibration curves which are different for raw sewages and final effluents. It is stated that 10 samples can be tested by the method within half an hour.

For plant control purposes, it is convenient, especially at small sewage plants with limited laboratory facilities, to estimate settle-able solids rather than suspended solids. This can be done by a simple volumetric method using an Imhoff Cone[1, 2] which consists of an inverted glass cone (1 litre capacity) having the apex part graduated in millilitres. A litre of the sample is settled (usually for 1 hour) and the volume of settled sludge is read and expressed as ml. per litre. Domestic sewages usually give readings of about 3–15 ml. of settleable solids and tank effluents a reading around 0·5 ml. Final effluents from the humus tanks at biological filtration plants should give much smaller values whilst activated sludge plant effluents should yield practically no settleable solids. The test can be used to give a rough idea of the efficiency of sedimentation tanks and, in the case of filter effluents, to indicate the amount of sludge