

## **Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes**

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# **Chapter 8 - ADVANCED INSTRUMENTAL ANALYSIS**

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*This chapter was prepared by R. Ballance.*

This chapter describes some of the more advanced instrumental methods which may be used for the determination of nutrients, major ions and trace elements, together with the analytical techniques for total, inorganic and organic carbon. Some of these techniques are particularly useful for the detailed analysis of sediments, particularly suspended sediments (see Chapter 13) and for the chemical analysis of biota (see Chapter 11). Although these techniques have been classified here as “advanced instrumental analysis” some, such as flame photometry, do not require expensive equipment and are often reliable and appropriate methods for water quality monitoring.

## **8.1 Atomic absorption spectrophotometry (AAS)**

Atomic absorption spectrophotometry is commonly used in many analytical laboratories for determination of trace elements in water samples and in acid digests of sediment or biological tissues.

### *Principle*

While a sample is being aspirated into a flame, a light-beam is directed through the flame into a monochromator and onto a detector that measures the amount of light absorbed by the atomised element in the flame. A source lamp composed of the element of interest is used because each element has its own characteristic wavelength. This makes the method relatively free from spectral or radiation interferences. The amount of energy at the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample over a limited concentration range. Most atomic absorption instruments are also equipped for operation in an emission mode.

### *Interferences*

Many metals can be determined by direct aspiration of sample into an air-acetylene flame. So called “chemical” interference occurs when the flame is not hot enough to dissociate the molecules or when the dissociated atoms are oxidised to a compound that will not dissociate further at the flame temperature. Such interferences can sometimes be overcome by adding specific elements or compounds to the sample solution. Dissociation of the molecules of silicon, aluminium, barium, beryllium and vanadium requires a hotter flame, and nitrous oxide-acetylene is used. Molecular absorption and light scattering caused by solid particles in the flame can cause high absorption values and consequently positive errors. Background correction techniques can be used to obtain correct values.

## *Apparatus*

√ Atomic absorption spectrophotometer consisting of a light source emitting the line spectrum of an element, a device for vaporising the sample, a means of isolating an absorption line and a photoelectric detector with its associated electronic amplifying and measuring equipment.

√ Burner. The most common type of burner is a premix, but the type of burner head recommended by the manufacturer of the spectrophotometer should be used.

√ Readout. Most instruments are equipped with either a digital or a null meter readout mechanism, and modern instruments have microprocessors capable of integrating absorption signals over time and linearising the calibration curve at high concentrations.

√ Lamps. Either a hollow cathode lamp or an electrodeless discharge lamp may be used. A separate lamp is needed for each element being measured.

√ Pressure-reducing valves are needed to reduce the high pressure of fuel and oxidant gases in the storage tanks to the controlled operating pressure of the instrument.

√ Vent. A vent located about 30 cm above the burner will remove fumes and vapours from the flame, thus protecting laboratory staff from toxic vapours and the instrument from corrosive fumes. An air flow rate is usually recommended by the manufacturer.

## *Reagents*

√ Air, cleaned and dried through a suitable filter to remove oil, water and other foreign substances.

√ Acetylene, standard commercial grade.

√ Metal-free water is essential for the preparation of all reagents and calibration standards.

√ Calcium solution. Dissolve 630 mg calcium carbonate,  $\text{CaCO}_3$ , in 50 ml of 1+5 HCl. If necessary, boil gently to obtain complete solution. Cool and dilute to 1,000 ml with water.

√ Hydrochloric acid, HCl, 1 per cent, 10 per cent, 20 per cent, 1+5, 1+1 and concentrated.

√ Lanthanum solution. Dissolve 58.65 g lanthanum oxide,  $\text{La}_2\text{O}_3$ , in 250 ml concentrated HCl. Add acid slowly until the material is dissolved and dilute to 1,000 ml with water.

√ Hydrogen peroxide, 30 per cent.

√ Nitric acid,  $\text{HNO}_3$ , 2 per cent, 1+1 and concentrated.

## *Preparation of standards*

Prepare standard solutions of known metal concentrations in water with a matrix similar to the sample. Standards should bracket the expected sample concentration and must be within the method's working range. Very dilute standards should be prepared daily from standard stock solutions having concentrations of at least 100 mg l<sup>-1</sup> (which can be obtained from commercial suppliers). If sample digestion is used, standards should be carried through the

same digestion procedures. The standard stock solutions described below have a concentration of 100 mg l<sup>-1</sup> (1.00 ml (100 µg)).

*Cadmium:* dissolve 0.100 g Cd metal in 4 ml concentrated HNO<sub>3</sub>, add 8 ml concentrated HNO<sub>3</sub> and make up to 1,000 ml with water.

*Calcium:* suspend 0.2497 g CaCO<sub>3</sub> in H<sub>2</sub>O, dissolve with a minimum of 1+1 HNO<sub>3</sub>, add 10 ml concentrated HNO<sub>3</sub> and make up to 1,000 ml with water.

*Chromium:* dissolve 0.1923 g CrO<sub>3</sub> in water, add 10 ml concentrated HNO<sub>3</sub>, make up to 1,000 ml with water.

*Copper:* dissolve 0.100 g Cu metal in 2 ml concentrated HNO<sub>3</sub>, add 10 ml concentrated HNO<sub>3</sub> and make up to 1,000 ml with water.

*Iron:* dissolve 0.100 g Fe wire in a mixture of 10 ml 1+1 HCl and 3 ml concentrated HNO<sub>3</sub>, add 5 ml concentrated HNO<sub>3</sub>, make up to 1,000 ml with water.

*Lead:* dissolve 0.1598 g Pb(NO<sub>3</sub>)<sub>2</sub> in a minimum of HNO<sub>3</sub> and make up to 1,000 ml with water.

*Magnesium:* dissolve 0.1658 g MgO in a minimum of 1+1 HNO<sub>3</sub>, add 10 ml concentrated HNO<sub>3</sub> and make up to 1,000 ml with water.

*Manganese:* dissolve 0.1000 g Mn metal in 10 ml concentrated HCl mixed with 1 ml concentrated HNO<sub>3</sub>, make up to 1,000 ml with water.

*Nickel:* dissolve 0.1000 g Ni metal in 10 ml hot concentrated HNO<sub>3</sub>, cool and make up to 1,000 ml with water.

*Potassium:* dissolve 0.1907 g KCl in water and make up to 1,000 ml with water.

*Sodium:* dissolve 0.2542 g NaCl in water, add 10 ml concentrated HNO<sub>3</sub> and make up to 1,000 ml with water.

*Tin:* dissolve 1.000 g Sn metal in 100 ml concentrated HCl and make up to 1,000 ml with water.

*Zinc:* dissolve 1.000 g Zn metal in 20 ml 1+1 HCl and make up to 1,000 ml with water.

### *Procedure*

It is not possible to provide an operating procedure that would be correct for all atomic absorption spectrophotometers because of differences between makes and models of instrument. The manufacturer's operating manual should be followed. A general procedure contains three components as described below.

#### *Zero the instrument*

1. Install a hollow cathode lamp for the desired element in the instrument and set the wavelength dial to the setting appropriate for the element.

2. Set the slit width according to the manufacturer's suggested value for the element being measured.
3. Turn on the instrument and adjust the lamp current to the level suggested by the manufacturer.
4. Let the instrument warm up, 10- 20 minutes, and readjust current as necessary.
5. Adjust wavelength dial until optimum energy gain is obtained.
6. Align lamp in accordance with the directions in the operating manual.
7. Install suitable burner head and adjust its position.
8. Turn on air. Adjust flow to the rate recommended to give maximum sensitivity for the metal being measured.
9. Turn on acetylene. Adjust flow to recommended rate, ignite and allow a few minutes for the flame to stabilise.
10. Aspirate a blank of deionised water that has been given the same treatment and acid concentration as the standards and samples.
11. Zero the instrument.
12. Aspirate a standard solution. Adjust the aspiration rate to obtain maximum sensitivity. Adjust the burner horizontally and vertically to obtain maximum response.

#### *Prepare calibration curve*

13. Select at least three concentrations of each standard metal solution. There should be one concentration greater and one less than that expected in the sample(s).
14. Aspirate a blank and zero the instrument.
15. Aspirate each standard in turn into the flame and record the absorbance.
16. Prepare a calibration curve by plotting the absorbance of the standards against their concentrations. This step is not necessary for instruments with direct concentration readout.

#### *Analysis of samples*

17. Rinse nebuliser by aspirating with water containing 1.5 ml HNO<sub>3</sub> per litre. Atomise blank and zero the instrument.
18. Atomise a sample and determine its absorbance.
19. Change lamps and repeat the procedure for each element.

#### *Calculation*

Refer to the appropriate calibration curves and determine the concentration of each metal ion, in  $\mu\text{g l}^{-1}$  for trace elements and in  $\text{mg l}^{-1}$  for the more common metals. Concentrations may be read directly from instruments with a direct readout capability. If a sample has been diluted, apply the appropriate dilution factor.

## 8.2 Gas chromatography

Gas chromatography is a highly sophisticated analytical procedure. It should be used only by analysts experienced in the techniques required and competent to evaluate and interpret the data.

### *Principle*

In gas chromatography (GC) a carrier phase (a carrier gas) and a stationary phase (column packing or capillary column coating) are used to separate individual compounds. The carrier gas is nitrogen, argon- methane, helium or hydrogen. For packed columns, the stationary phase is a liquid that has been coated on an inert granular solid (the column packing) that is held in a length of borosilicate glass tubing. The column is installed in an oven with the inlet attached to a heated injector block and the outlet attached to a detector. Precise and constant temperature control of the injector block, oven and detector is maintained. Stationary phase material and concentration, column length and diameter, oven temperature, carrier gas flow and detector type are the controlled variables.

When the sample solution is introduced into the column the organic compounds are vaporised and moved through the column by the carrier gas. They travel through the column at different rates depending on differences in partition coefficients between the mobile and stationary phases.

### *Interferences*

Some interferences occur because of sample, solvent or carrier gas contamination or because large amounts of a compound were injected into the GC and some of it lingered in the detector. Methylene chloride, chloroform and other halocarbon and hydrocarbon solvents are frequent contaminants. These solvents should not be used anywhere in the vicinity of the equipment. Another contaminant is sulphur; interference may be eliminated by adding a small amount of copper filings or mercury to samples to precipitate sulphur as metallic sulphide.

There may also be sources of interference within the equipment itself. Septum bleed occurs when silicon compounds used in the construction of the septum on the injection port "bleed" from the heated septum. This can be prevented by septum sweep - passing clean carrier gas over the septum to flush out bleed compounds. Column bleed can occur when column temperatures are high and water or oxygen is introduced into the system. Solvent injection can damage the stationary phase and some organic compounds can degrade the column coating. Injection of certain surface-active agents can completely destroy GC columns.

Ghost peaks can occur because a sample that has been passed through the system contained either a large quantity of a given compound or a compound that adsorbed to the column coating. Measurements on subsequent sample(s) will show a peak resulting from the residue of the previous sample. This can be avoided by selecting a column coating that precludes such interactions or by flushing out the system with a solvent blank between samples.

### *Detectors*

Various types of detector are available for use with GC systems. Brief descriptions of some of these are provided here for general information.

The *electrolytic conductivity detector* contains reference and analytical electrodes, a gas-liquid contactor and a gas-liquid separator. The conductivity solvent enters the cell and flows by the reference electrode. It combines with the gaseous reaction products in the gas-liquid contactor. This mixture is separated into gas and liquid phases in the gas-liquid separator with the liquid phase flowing past the analytical electrode. The electrometer monitors the difference in conductivity between the reference electrode and the analytical electrode. Only organic compounds containing halogen, nitrogen, sulphur or nitrosamine can be detected in this way.

The *electron capture detector* (ECD) is operated by passing the effluent from the gas chromatographic column over a radioactive beta-particle emitter, usually nickel-63 or tritium, adsorbed on platinum or titanium foil. An electron from the emitter ionises the carrier gas and produces a burst of electrons. About 100 secondary electrons are produced for each initial beta-particle. After further collisions the energy of these electrons is reduced to the thermal level and they can be captured by electrophilic sample molecules. The electron population is collected by applying a voltage pulse to the cell electrodes, and the pulse interval is automatically adjusted to maintain a constant current. The change in the pulse rate when a sample enters the detector is related to the concentration of contaminant in the sample. The detector is highly sensitive to molecules containing halogens, peroxides, quinones and nitro groups but is insensitive to functional groups such as amines, alcohols and hydrocarbons.

The *flame ionisation detector* (FID) consists of a small hydrogen/air diffusion flame burning at the end of a jet. When organic compounds enter the flame from the column, electrically charged intermediates are formed. These are collected by applying a voltage across the flame; the resulting current is measured after amplification by an electrometer. The FID is sensitive to nearly all organic carbon-containing compounds but does not respond to carrier gas impurities such as water and carbon dioxide. It has a wide linear response range, is relatively insensitive to small changes in flow rate, and is reliable, rugged and easy to use. It is, however, a destructive detector that changes irreversibly the physical and chemical characteristics of the sample. Nevertheless, the FID is probably the most widely used detector for gas chromatography.

The *photoionisation detector* (PID) detects organic and some inorganic species in the effluent of a gas chromatograph, with detection limits in the picogram range. The detector is equipped with an ultraviolet light source that emits photons that pass through an optically transparent window into an ionisation chamber where they are absorbed by the eluted species. Compounds with ionisation potential less than the UV source are ionised. A positively biased high-voltage electrode accelerates the resulting ions to a collecting electrode. An electrometer measures the resulting current, which is proportional to the concentration of the eluted species. The PID has high sensitivity, low noise and excellent linearity, is non-destructive and can be used in series with a second detector for a more selective detection.

The *mass spectrophotometer* (MS) has the ability to detect a wide variety of compounds, coupled with the capacity to deduce compound structures from fragmentation patterns. It detects compounds by ionising molecules into charged species with a 7-eV beam. The ions are accelerated towards a quadrupole mass filter through a series of lenses and the differently sized charged fragments are separated according to mass-to-charge ratio. A computer control permits fragments of only one mass-to-charge ratio to pass at any one time and be detected by an electron multiplier. Most chemicals have a unique fragmentation pattern (mass spectrum), and the computer searches an internal library of known mass spectra to identify an unknown compound exhibiting a particular spectrum.

## *Procedure*

It is not possible to provide a procedure for gas chromatography that would be applicable to all of the commercially available instruments. The instruction manual supplied by the manufacturer will deal with the specific characteristics of the particular model to which it refers. It must be emphasised that the technique is sophisticated and technicians should undergo a period of training in the use of the equipment. Appropriate training can normally be provided by the manufacturer of the equipment.

## **8.3 Flame photometry**

Flame photometry makes possible the determination of trace amounts of lithium, potassium, sodium and strontium, although other methods of analysis for lithium and strontium are preferred.

### *Principle*

The sample, after dilution if necessary, is sprayed into a butane- air or propane- air flame. The alkali metals absorb energy from the flame and become raised to an excited energy state in their atomic form. As these individual atoms "cool" they fall back into their original unexcited or ground state and re-emit their absorbed energy by radiation of specific wavelengths, some of which are within the visible region of the electromagnetic spectrum. This discrete emission is isolated by an optical filter and, for low concentrations, is proportional to the number of atoms returning to the ground state. This, in turn, is proportional to the number of atoms excited and, hence, to the concentration of the element in the solution.

### *Minimum detectable concentration and range*

The minimum detection level for both potassium and sodium is approximately  $100 \mu\text{g l}^{-1}$ . The upper limit is approximately  $10.0 \text{ mg l}^{-1}$ , but this may be extended by diluting the samples.

### *Apparatus*

√ Flame photometer, either direct reading or internal standard type, or an atomic absorption spectrophotometer in the flame emission mode.

√ Normal laboratory glassware. Rinse glassware with 1+15  $\text{HNO}_3$  followed by several flushes with deionised distilled water.

### *Reagents*

√ Deionised distilled water. Use deionised distilled water to prepare all calibration standards and reagents and as dilution water.

√ Stock sodium solution. Dissolve 2.542 g NaCl dried at  $140^\circ\text{C}$  and dilute to 1,000 ml with water ( $1.00 \text{ ml} \equiv 1.00 \text{ mg Na}$ ).

√ Intermediate sodium solution. Dilute 10.00 ml stock sodium solution to 100 ml with water ( $1.00 \text{ ml} \equiv 100 \mu\text{g Na}$ ). This solution is used to prepare the calibration curve in the range 1 to  $10 \text{ mg l}^{-1}$  sodium.

√ Standard sodium solution. Dilute 10.00 ml intermediate sodium solution to 100 ml with water (1.00 ml  $\equiv$  10.0  $\mu\text{g Na}$ ). This solution is used to prepare the calibration curve in the range 0.1 to 1.0  $\text{mg l}^{-1}$  sodium.

√ Stock potassium solution. Dissolve 1.907 g KCl dried at 110 °C and dilute to 1,000 ml with water (1.00 ml  $\equiv$  1.00 mg K).

√ Intermediate potassium solution. Dilute 10.00 ml stock potassium solution to 100 ml with water (1.00 ml  $\equiv$  100  $\mu\text{g K}$ ). This solution is used to prepare the calibration curve in the range 1 to 10  $\text{mg l}^{-1}$  potassium.

√ Standard potassium solution. Dilute 10.00 ml intermediate potassium solution to 100 ml with water (1.00 ml  $\equiv$  10.0  $\mu\text{g K}$ ). This solution is used to prepare the calibration curve in the range 0.1 to 1.0  $\text{mg l}^{-1}$  potassium.

### *Procedure*

It is impossible to provide detailed operating instructions that would be universally correct because of differences between the various models of instruments made by different manufacturers. Follow the recommendations contained in the operating manual supplied with the instrument. Select the correct photocell and wavelength (589 nm for sodium, 766.5 nm for potassium), slit width and sensitivity, and fuel and air (or oxygen) pressures. Follow recommended steps for warm-up, making corrections for interferences and flame background, rinsing of burner, igniting of sample and measuring emission intensity.

### *Calibration*

1. Prepare a blank and a stepped set of sodium calibration standards in the range 0 to 1.0  $\text{mg l}^{-1}$  or 0 to 10.0  $\text{mg l}^{-1}$  as appropriate.
2. Starting with the highest calibration standard and working towards the blank, measure emission at 589 nm. Repeat this step enough times to obtain a reliable average reading for each calibration standard.
3. Construct a calibration curve from the sodium standards.
4. Prepare a blank and a stepped set of potassium calibration standards in the range 0 to 1.0  $\text{mg l}^{-1}$  or 0 to 10.0  $\text{mg l}^{-1}$  as appropriate.
5. Starting with the highest calibration standard and working towards the blank, measure emission at 766.5 nm. Repeat this step enough times to obtain a reliable average reading for each calibration standard.
6. Construct a calibration curve from the potassium standards.

### *Measurement*

7. Spray a sample into the flame and measure emission at 589 nm. Repeat enough times to obtain a reliable average value. Determine the concentration of sodium from the sodium calibration curve.
8. Spray a sample into the flame and measure emission at 766.5 nm. Repeat enough times to obtain a reliable average value. Determine the concentration of potassium from the potassium calibration curve.



### *Precision and bias*

A synthetic sample containing sodium 19.9 mg l<sup>-1</sup>, potassium 3.1 mg l<sup>-1</sup>, calcium 108mg l<sup>-1</sup>, magnesium 82 mg l<sup>-1</sup>, chloride 241 mg l<sup>-1</sup>, nitrite nitrogen 0.25 mg l<sup>-1</sup>, nitrate nitrogen 1.1 mg l<sup>-1</sup>, sulphate 259 mg l<sup>-1</sup> and total alkalinity 42.5 mg l<sup>-1</sup> was analysed in 35 laboratories by the flame photometric method with the following results:

Sodium: relative standard deviation 17.3 per cent, relative error 4.0 per cent.

Potassium: relative standard deviation 15.5 per cent, relative error 2.3 per cent.

## **8.4 Total, organic and inorganic carbon**

The following definitions apply to this procedure:

- Total carbon (TC) is all of the carbon present as dissolved matter and/or in suspension in the water.
- Total inorganic carbon (TIC) is all of the carbon present as inorganic matter, dissolved and/or in suspension in the water.
- Total organic carbon (TOC) is all of the carbon present as organic matter, dissolved and/or in suspension in the water.

Measurement of TOC is a much more rapid means of determining the organic content of water and wastewater than is the measurement of biochemical oxygen demand (BOD). In addition, two of the methods also provide more rapid measurement than the chemical oxygen demand (COD) test. Because of the presence of non-biodegradable organic compounds, BOD is not directly related to total organic carbon, and COD analyses may include reduced inorganic compounds. However, if the relative concentrations of organic compounds in the samples do not change greatly, empirical relationships can be established between TOC and BOD or COD to permit speedy and convenient estimations of the latter. Measurement of TOC can be used to monitor processes for the treatment or removal of organic contaminants without undue dependence on the oxidation states, and is valid at low concentrations.

The concentration of organic carbon present in surface water is generally less than 10 mg l<sup>-1</sup>, except where a high concentration of municipal or industrial waste is present. Higher levels of organic carbon may be encountered in highly coloured water, and water collected from swamps may have organic carbon concentrations exceeding 100 mg l<sup>-1</sup>. For municipal wastewater treatment plants, influent TOC concentrations may reach several hundred milligrams per litre, but effluent concentrations from a secondary treatment facility are typically less than 50 mg of organic carbon per litre.

### *Sample handling*

Collect and store samples in bottles made of glass, preferably brown. Plastic containers are acceptable after tests have demonstrated the absence of extractable carbonaceous substances. Samples that cannot be examined promptly should be protected from decomposition or oxidation by preservation at 0- 4 °C, minimal exposure to light and atmosphere, or acidification with sulphuric acid to a pH not greater than 2. Storage time should be kept to a minimum under any conditions. It should not exceed seven days and, depending on the type of sample, even shorter storage may be indicated.

## *Methods*

So many techniques and types of equipment exist for the analysis of organic carbon that it is impossible to recommend a procedure applicable in all situations. The advice that follows is that given by the French Standardisation Association (Association Française de Normalisation (AFNOR), Paris) for selection of an appropriate analytical procedure. Sections 8.4.1, 8.4.2 and 8.4.3 describe how some of these recommendations are related to the type of water to be analysed.

## *Principle*

The principle of all methods for the determination of total carbon (TC) in water is oxidation of the carbon to carbon dioxide (CO<sub>2</sub>). Oxidation may be carried out by combustion, chemical reaction by the wet method using appropriate oxidising agents, UV irradiation or any other appropriate procedure. The carbon dioxide formed may be determined directly, or indirectly following reduction to another component (methane, for example).

Various analytical methods have been suggested, some of which are:

- IR spectrometry,
- volumetric determination,
- thermal conductivity,
- conductimetric measurement,
- coulometric measurement,
- specific CO<sub>2</sub> electrode,
- flame ionisation following methanisation.

### *Principal forms of carbon in water*

A water sample may contain variable amounts of:

- dissolved and particulate organic carbon,
- organic carbon originating from more or less volatile substances, and
- dissolved mineral carbon (carbonates, carbon dioxide) and particulate carbon (active charcoal).

The different matrices of the specimens that result from the presence of these forms of carbon in variable proportions must be taken into consideration before the analysis, because they largely determine what apparatus and procedure to select.

### *Selection of procedure in relation to the matrix of the sample*

#### A. Presence of dissolved carbonates and carbon dioxide

When the carbon derived from dissolved carbonates and CO<sub>2</sub> is considerably in excess of the TOC, estimation by the separate measurement of total carbon and mineral carbon to arrive at the arithmetic difference may be somewhat inaccurate because of the errors connected with each measurement. Carbonates and CO<sub>2</sub> may be eliminated by acidification at pH 1 with H<sub>3</sub>PO<sub>4</sub> followed by degassing in a stream of gas which is free of CO<sub>2</sub> and organic components. Thereafter, TOC is determined in the degassed sample. In this case it is important to check the efficiency of the degassing apparatus of each user (gas flow, duration of degassing and geometry of the degasser).

## B. Presence of particulate mineral carbon and suspended matter

Using the proposed techniques, it is impossible to ensure total oxidation of particles by low-temperature wet methods. In addition, the difficulties inherent in the sampling of heterogeneous media still persist.

## C. Presence of volatile substances

Pretreatment by degassing modifies the initial composition of the sample by almost completely eliminating the volatile components. The presence of surfactants may interfere with degassing.

## D. Presence of dissolved mineral matter

Depending on the method used, the dissolved mineral load may interfere with the operation of the apparatus (for example, the sooting of UV lamps in the photochemical technique; clogging of the catalytic mass of the furnaces in high-temperature and low-temperature oxidation procedures; precipitation of calcium salts; release of chlorine resulting from the oxidation of chlorides).

*Note:* Depending on the method, the carbon present in some inorganic compounds (cyanides, cyanates, thiocyanates, carbon disulphide, etc.) will be regarded as organic carbon.

## E. Effect of the nature of the inorganic matter

The oxidation of organic matter is related to its structure, and the degree to which complete oxidation is achieved will depend on the analytical method used.

### *Apparatus*

√ Ordinary laboratory glassware. All the glassware used must be kept perfectly clean in order to limit contamination and must be reserved exclusively for this determination. Regular verification of the quality of the glassware using water of satisfactory purity is needed to restrict contamination by "dirty" glassware. Several cleaning techniques have proved to be effective, including the following:

(i) Leave glassware to soak for several (4- 12) hours in a chromic acid mixture (concentrated  $\text{H}_2\text{SO}_4$  saturated in  $\text{K}_2\text{Cr}_2\text{O}_7$ ) or an effective laboratory detergent solution.

(ii) Rinse copiously with the water used to prepare the reagents.

(iii) Allow to dry away from dust, and keep the containers closed.

Should this treatment be inadequate, non-graduated glassware may be raised to a temperature of 350- 400 °C for 2 hours in an oxidising atmosphere.

Apparatus for determination of TOC must be set up in a way that will limit outside contamination by carbonaceous compounds.

## Reagents

All the reagents must be of recognised analytical quality. The total concentration of carbon in the water used for dilution and to prepare the standards must be negligible by comparison with the total carbon of the sample and the standards.

√ Stock solution of potassium hydrogen phthalate with a carbon content of  $1,000 \text{ mg l}^{-1}$ . In about 700 ml of fresh distilled water in a 1-litre volumetric flask, dissolve 2.125 g of potassium hydrogen phthalate,  $\text{C}_8\text{H}_5\text{KO}_4$ , that has first been dried for 2 hours at a temperature not exceeding  $120 \text{ }^\circ\text{C}$ . Make up to the 1-litre mark with distilled water. This solution is stable for about a month if stored at  $4 \text{ }^\circ\text{C}$  in a stoppered, opaque glass bottle.

√ Calibration solutions. These solutions, which must be made up daily, are prepared by diluting the stock solution of potassium hydrogen phthalate.

√ Control solution with a carbon content of  $1,000 \text{ mg l}^{-1}$  for determination of total inorganic carbon. In a 1,000-ml graduated flask containing 500 ml of water, dissolve 4.42 g of sodium carbonate,  $\text{Na}_2\text{CO}_3$ , that has first been dried at  $120 \text{ }^\circ\text{C}$  for 1 hour. Add 3.497 g of sodium bicarbonate,  $\text{NaHCO}_3$ , that has been stored in a desiccator, and make up to 1,000 ml with water. This solution remains stable for about 1 month at  $4 \text{ }^\circ\text{C}$ .

√ Concentrated phosphoric acid,  $\text{H}_3\text{PO}_4$ . Used to acidify the sample before degassing (in general 2 to 3 drops in 20 ml of water).

√ Gases. The gases used must be free of  $\text{CO}_2$  and organic impurities.

## Procedure

1. Follow the manufacturer's instructions for the use of the equipment in the analysis of TOC. Before TOC is measured, care must be taken to ensure that the control tests are carried out at least as frequently as recommended by the manufacturer.

2. The equipment must be calibrated daily. A calibration curve is produced by the use of potassium hydrogen phthalate solutions at appropriate concentrations (4 or 5 points for each measurement range when the equipment permits).

3. As with all measurements made by instruments, there are many variables that affect the total response of the system. The two main variables to be verified for all technologies are oxidation chemistry and detection. In the first of these, because of the disparity of the physicochemical principles involved, no general rules for verificatory procedures can be given. For the second, the course of the process may be assessed by computer visualisation of the output signal (background noise, shape of peak, return to base-line and replicability).

## Calculation of the results

Determine the concentrations of TOC in the specimens using the calibration curve or the data processing system for the instrument concerned.

### 8.4.1 Surface waters and water intended for human consumption or domestic use

The characteristics of surface waters and water intended for human consumption or domestic use are: low TOC concentrations (of the order of  $0.1$  to  $10 \text{ mg l}^{-1}$ ), with the proportion of the carbon derived from volatile organic compounds generally being slight as compared with TOC, a content of dissolved salts that does not appreciably affect the

operation of the apparatus, a concentration of mineral carbon (carbonates and bicarbonates) that is generally greatly in excess of the TOC, and small amounts of suspended matter.

#### *Choice of technique*

For TOC concentrations greater than 2 mg l<sup>-1</sup>, any of the various analytical procedures is acceptable provided that normal care is used in their performance. Precise measurement of TOC is more difficult for concentrations below 2 mg l<sup>-1</sup>. Laboratory experience has shown that, of the apparatus currently available, photochemical systems are preferable for analysis of waters of the type under consideration. The contribution of carbon derived from volatile organic compounds (carbon usually less than 1,000 µg l<sup>-1</sup>) may be regarded as insignificant compared with measurement errors.

In methods that depend on the difference between TC and TIC, the measurement errors for TC and TIC are at least 5 per cent for waters containing about 50 mg TC per litre or about 200 mg of carbonates per litre. Consequently the calculated value of TOC (TC - TIC) will not agree with the measured value of TOC.

#### **8.4.2 Seawater or water with a high content of dissolved salts**

These recommendations are applicable to seawater or water with a high content of dissolved salts. The characteristics of these waters are: a high chloride content, a low TOC concentration, and a high TIC concentration.

#### *Choice of technique*

The main difficulty arises from the presence of chlorides which interfere with the operation of the apparatus, either by the destruction of catalyst masses and corrosion of high-temperature furnaces, or by considerable modification of oxidation kinetics in photochemical oxidation techniques that necessitate the use of a special oxidising medium.

In general, the addition of a soluble mercury salt is recommended to complex the chlorides and thus prevent their oxidation.

#### **8.4.3 Wastewater and surface water with a high TOC content**

These recommendations apply to wastewater and surface waters with a high TOC content. The characteristics of these waters are: a high content of organic matter, a large amount of suspended matter, and more frequent presence of volatile compounds.

#### *Choice of technique*

The main difficulty arises from suspended matter because of the heterogeneity of the medium (which makes representative sampling a difficult operation when the volume of the analytical sample is small) and mechanical incompatibility of solid particles with some parts of the apparatus (valves, etc.).

Recognising the diverse origins of organic matter, some substances, especially in suspension, may prove difficult to oxidise by photochemical oxidation techniques (incomplete oxidation is often revealed by protracted peaks). It is sometimes possible to overcome this problem by modifying the oxidising medium and increasing the length of the reaction time. No clear choice of technique is possible. However, techniques employing a high-temperature furnace system are usually best.

## 8.5 Source literature and further reading

AFNOR 1987 *Guide pour la Détermination du Carbone Organique Total*. Association Française de Normalisation, Paris (T90-102).

APHA 1992 *Standard Methods for the Examination of Water and Wastewater*, 18th edition. American Public Health Association (APHA), American Water Works Association (AWWA) and Water Pollution Control Federation (WPCF), Washington, DC.

ISO 1990 *Water Quality - Guidelines for the Determination of Total Organic Carbon (TOC)*. International Standard ISO 8245, International Organization for Standardization, Geneva.

WHO 1992 *GEMS/WATER Operational Guide*. Third edition, Unpublished WHO document GEMS/W.92.1, World Health Organization, Geneva.

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