The International Norm for the Measure of the TOC and The Carbons in Waters Chronological and Critical Analysis

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Introduction

The presence of organic matter in waters has always attracted the attention of researchers. The matrix variety brings to consider with a different attention and interest both dissolved and suspended compounds. Lastly the interest to apply the analysis by "global indicators" has an increasing trend for both pollution and quality checking. Among these indicators, TOC (Total Organic Carbon) is recognised as very useful to obtain quantitative and qualitative informations from both the absolute value and the variation trend.

Really, TOC is due to natural and antropic sources the latter being more responsible of dangers for human health, thence the importance of its determination in all kind of waters. It has to be considered that TOC depends on the type of the considered water, but it is also affected by several parameters such as temperature, salinity, pH, microbial activity, surrounding vegetation; as a consequence, TOC value is highly variable: from less than 1 mg/l in underground or sea waters, to 2-10 mg/l in lake or river waters, up to 100 mg/l in marshes and fens [1]. Other points of useful interpretation concern the stability of TOC value during the time and the investigation and knowledge of the compounds accounted for its value.

European Normative give guidelines for the correct determination of organic carbon. Definitions, interferences, reagents, and some pretreatment of water samples are generally dealt for ground water, surface water, sea water and waste waters (TOC content ranging from 0.3 mg/L to 1000 mg/L) while lower values are foreseen only in special cases such as, for example, drinking water or ultrapure water for electronic (microprocessors) and drug industries. In these cases a very sensitive instrument is needed.

The commercially available instruments usable for TOC measurement differ for the nature of the oxidising process and/or for detector type. The oxidation process can be mainly run by two methods; high-temperature pyrolysis system, and low-temperature photochemical system. Three low-temperature photochemical oxidative systems are commercially available: ultraviolet irradiation, heated persulfate, and persulfate/UV.

The final determination of CO_2 is carried out by different analytical procedures, for example: Infrared spectrometry, acid-base titration (preferably in non-aqueous solution), thermal conductivity, conductometry, coulometry, CO_2-sensitive sensors and flame ionisation - used after reduction of the CO_2, among others, to methane.

The Total Organic Carbon

In all the countries the analysis of Total Organic Carbon (TOC) is recognised as the more suitable parameter for the control of civil and industrial wastes.

Total Organic Carbon (TOC) is an indirect measure, as carbon, of organic molecules present in waters, this means that we can have an aspecific datum that gives no informations about the nature of the organic matter.

In unpolluted waters TOC is mainly due to humic substances and to vegetal and animal partially degraded matter (generally resistant to microbial degradation). Lignin, fulvic acids and tannins are the most abundant compounds; although not well chemically defined, these compounds can be considered as complex polyphenols with some characters typical of carbohydrates. These natural materials show a complexing capacity towards heavy metals that can heavily affect their solubility, the metal concentrations can so rise up to toxic levels even if it is possible an increase of the unbioavailable species.

In polluted waters TOC is mostly due to antropic contributions, such as fertilizers, pesticides, surfactants, solvents coming from their direct use or from inefficient sewage disposal plants.

A number of acceptable methods exist for analysing TOC; all are based on a theoretically quantitative process of oxidation of the organic matter contained in the tested solution and an instrumental detection of the produced carbon dioxide that results stoichiometrically related to TOC. Unfortunately different organic molecules are completely oxidised in different experimental conditions due to their different recalcitrance, so easy degradable molecules are quantitatively oxidised also in mild experimental conditions while the most recalcitrant, that are generally the more toxic, require more drastic conditions. The above said complex composition of waters to be subjected to TOC test forces the analytical technology toward instruments able to ensure a complete oxidation (mineralisation to CO_2) of all the possible organic compounds.

It is to be taken into account that water matrices surely contain also inorganic carbon (dissolved CO_2, carbonate and bicarbonate) so, all methods must discriminate between the inorganic carbon and CO_2 produced from the oxidation of organic molecules in the sample.

Two general approaches are used to measure TOC. One approach determines TOC by subtracting the measured total inorganic carbon (TIC) from the measured total carbon (TC), which is the sum of organic carbon and inorganic carbon:

$$TOC = TC - TIC$$

The other approach first purges the TIC from the sample before any organic carbon measurement is performed. However, this TIC purging step also purges some of the organic molecules (purgeable organic substance, such as benzene, toluene, cyclohexane, and chloroform may partly escape on stripping), which can be retrapped and oxidised to CO_2 and quantified as purgeable organic carbon (POC). The remaining organic matter in the sample is also oxidised to CO_2 and quantified as non-purgeable organic carbon (NPOC). In this approach, TOC is the sum of POC and NPOC:

European Norm From 1973 to 1999

Many countries ruled the determination of TOC in order to avoid that builders of scientific equipment manage at their commercial convenience on this field and, actually, builders must now follow rules imposed by internationally recognised organisms.

Since 1970 the scientific community recognised the problems related to the TOC measurement in aqueous matrices. Actually we have a lot of guidelines, often different and/or conflicting, concerning the nature of the matrix or the analytical method to be applied; a non exhaustive list is presented in following table.

The newest rules impose the use of recalcitrant molecules as test solutions in order to control if a quantitative conversion to CO_2 (mineralisation) occurs. This is a good choice as, in such a way, the instruments, the methods, the sensor are stressed and it is not easy to obtain a correct TOC value. In Fig. 1 we show one of the most used molecules imposed by the new rules [2], if obtained it guarantees accuracy in TOC tests.
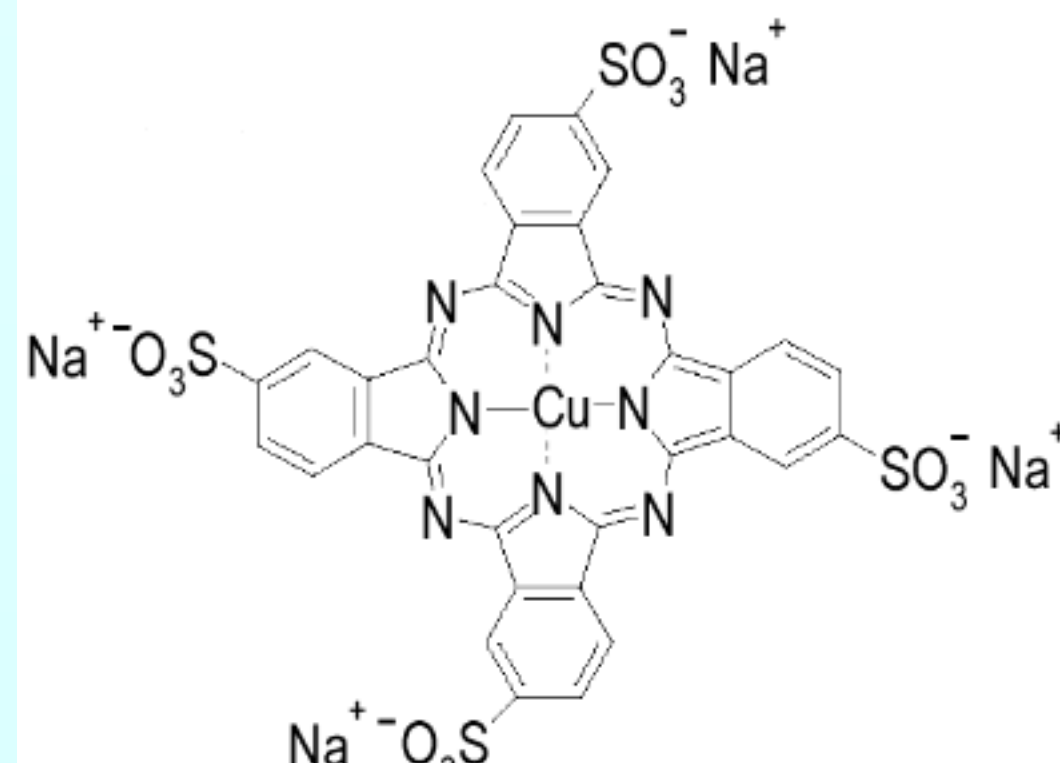
1. **AOAC** (Association of Official Analytical Chemists) Official Method 973.47. First version 1973. Carbonaceous material of water sample is oxidised to CO_2 in stream of O_2 or air in catalytic combustion tube at 950° C. Calibrated IR analyser measures CO_2, the method is applicable to 1-150 mg organic C in surface and saline waters and domestic and industrial wastes.
2. **DIN** (Deutsche Institut für Normung eV) Method 38 409. Last version 1983. It is a German standard method for waste water and muds analysis.
3. **ISO** (International Organization of Standardization) Method 8245. Version 1987. It is a guideline for TOC analysis the last version of which is the ISO/CEN EN 1484 (1997).
4. **ASTM** (American Society for Testing and Materials) Method D4839. It was emitted in 1988. It is about TC (Total Carbon), TOC and IC (Inorganic Carbon) determination in waste water, sea water in the range 0.1 mg/L and 4000 mg/L of C, by UltraViolet or Persulfate Oxidation or both and CO_2 infrared detection.
5. **ASTM Method D4779.** It was made in 1988. This method is about TC, TOC, IC determination by UltraViolet or Persulfate Oxidation or both and CO_2 infrared detection. It is different from previous because it examines different matrixes: makeup water, high purity process water such as demineralised effluent, condensed and electronic grade rinse water. The tested concentration ranges is from 50 to 1000 mg/L of C.
6. **ASTM Method D2579.** This method was emitted in 1985, modified in 1989 and covers the determination of TOC in waste water including brackish water and brines. The tested concentration ranges is from 2 to 200 mg/L. Are included the Method A (Oxidation-IR detection) and Method B (Reduction-Flame Ionization detection).
7. **ASTM Method D4129.** It was emitted in 1989 and modified in 1999. This method applies to TOC determination by thermal oxidation using high temperature combustion to convert organic material into carbon dioxide. Carbon dioxide produced is measured by coulometric method. The useful concentration ranges is between 2 and 20000 mg/L (for high concentrations).
8. **Standard Method (SM) 5310 A.** Last change in 1992. Introduction on TOC analysis. Organic carbon in water and waste water is composed by a variety of organic compounds in various oxidation states. Some of those organic matter may be futherly oxidised by biochemical or chemical process and Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) can be used to characterise their fractions. If a reproducible relationship can be established among TOC, COD and BOD, then TOC can be used for estimating also BOD and COD.
9. **SM 5310 B.** Combustion-Infrared method. Last change in 1992. It is used for a wide variety of samples, but its accuracy is dependent on particle size reduction because it uses orifice syringes. Sample is homogenised and diluted. A microportion is injected into a heated reaction chamber (900° C) packed with an oxidant catalyst such as cobalt oxide. CO_2 produced by oxidation of carbon is transported into a NDIR. TOC is determinate by the difference TC-IC. Minimum detectable concentration is 1mg/L of C).
10. **SM 5310 C.** UV/ persulphate oxidation method. Last change in 1992. This method uses Sodium Persulphate as oxidant and heat or UV activation of the reagents. This method is rapid and precise for trace levels of organic matter in water. CO_2 generated is measured by NDIR. Minimum detectable concentration is 0.05 mg/L of C but careful attention must be pay to minimising sample contamination.
11. **SM 5310 D.** Wet oxidation method. Last change in 1992. Reagent is the granular potassium persulphate, heat is used for activation of the reagents and there is NDIR detection of CO_2. This method is suitable for the analysis of water suspended sediment mixture, brines and waste water containing at least 0.1 mg/L of C as non Purgeable Organic Carbon (NPOC).
12. **IRSA** (Istituto di Ricerca sulle Acque) Method 5040. This method assumed official form to check and sample waste water when Merli's law was issued (10 May 1976 nr.319). Even the legislative decree (25 January 1992 n.130 - according to the fitness of fresh water to sea life) established to follow the analytical and sampling method published by IRSA. However this normative law was deleted from legislative decree number 152/99 and it only can be used as an analytical technique or as a sampling method.
13. **UNICHIM** (Associazione per l'unificazione nel settore dell'industria chimica, federata UNI-Ente Nazionale Italiano di Unificazione) Method 944.1995. This method regards water to be used for human consumption. It is a physical and chemical methodology based on traditional analytical techniques.
14. **April 1997 DRAFT.** Suggestion as a CEN Enquiry drawn up by Technical Committee CEN/TC292 "Characterization of waste" by NNI (National Nanotechnology Initiative). This method is used for the determination of organic matter in waste water and may be used for assessing the suitability of waste for land filling.
15. **Standard ISO/CEN prEN 1484 (Guideline).06/04/1997.** This European Standard was approved by the ISO/CEN and by the European Parliament. It was prepared by Technical Committee CEN/TC 230 Water analysis by DIN. It gives guidance for the determination of Organic in drinking water, ground water, sea water, waste water. The tested concentration ranges is between 0.3 and 1000 mg/L of C. The instrument specification should at least be suitable to measure particles of 100 microns size.
16. **USP- United States Pharmacopoeia 23/ 643.** TOC and Conductivity.1998. This method is used for the determination of organic pollution in Purified Water (PW) and in Water for Injection (WFI) where minimum detectable concentration is 0.05 mg/L of TOC as C.
17. **EPA** (U.S. Environmental Protection Agency) Method 415.1 dated 1999. This method regards TOC determination by combustion or oxidation.
18. **EPA Method 415.2 dated 1999.** This method is used for the analysis of organic carbon. It is based on UV promoted persulphate oxidation. It covers determination of organic carbon in drinking water and other matrix. It is applicable for carbonaceous matter of particle size of 0.2 mm or less in a range from 0.0050 to 10 mg/L of C.
19. **EPA SW 846 Method 9060.** Last change 1999. SW 846 are Test Methods for Evaluating Solid Waste (Office of Solid Waste and Emergency Responce). This method is used for organic carbon determination in ground and sediments. It uses high-temperature pyrolysis system in the presence of oxygen.

Fig. 1, Copper phthalocyanine-tetrasulfonic tetrasodium salt (C32H12CuN8O12S4Na4) suggested by the EN1484 as "test molecule" for TOC analysers due to its recalcitrance to oxidation processes. Moreover, it can poison catalytic beds, leaves salts in reaction cell, produce SOx and NOx as degradation products interfering in the measure..

CO₂ Detectors

A TOC measurement requires an instrumental apparatus consisting of, mainly, two parts: the first must ensure the mineralisation of the organic content in the sample, the second (detector) have to measure the produced CO_2. The same attention spent to obtain a CO_2 amount stoichiometric with TOC has to be spent to obtain its correct detection. The detector has to be carefully chosen, according to the matrix under test, in order to ensure suitable values for the analytical parameters (reproducibility, accuracy, selectivity, sensitivity, limit of detection).

Many analytical methods are available for the carbon dioxide analysis and we here list the most used.

IR Detector

Infrared (IR) absorption (or reflection for solids) is a widely used spectroscopic technique that can be successfully applied also for a continuous monitoring of chemical process.

The IR wavelength region ranges from 800 to 15384 nm but, generally, the commercially available instruments can operate in the near IR (800 to 2500 nm) or in the mid IR (2500 to 15384 nm).

Among the detectors used in TOC analysers, the most common detector is the non-dispersive IR analyser (NDIR), which operate in the mid IR as, at this high wavelengths, interference from IR-absorbing gases (CO, NO, SO_2 and NH_3) are minimised. It measures the infrared light absorbed by carbon dioxide as it passes through a flow-through IR absorption cell

Carbon dioxide produced by the sample degradation flows through the sample cell and absorbs the IR light. The IR spectra is shown in Fig. 2; it can be seen the characteristic wavelengths corresponding to the CO_2 absorption and the main possible interferent that results to be the water vapour [3].
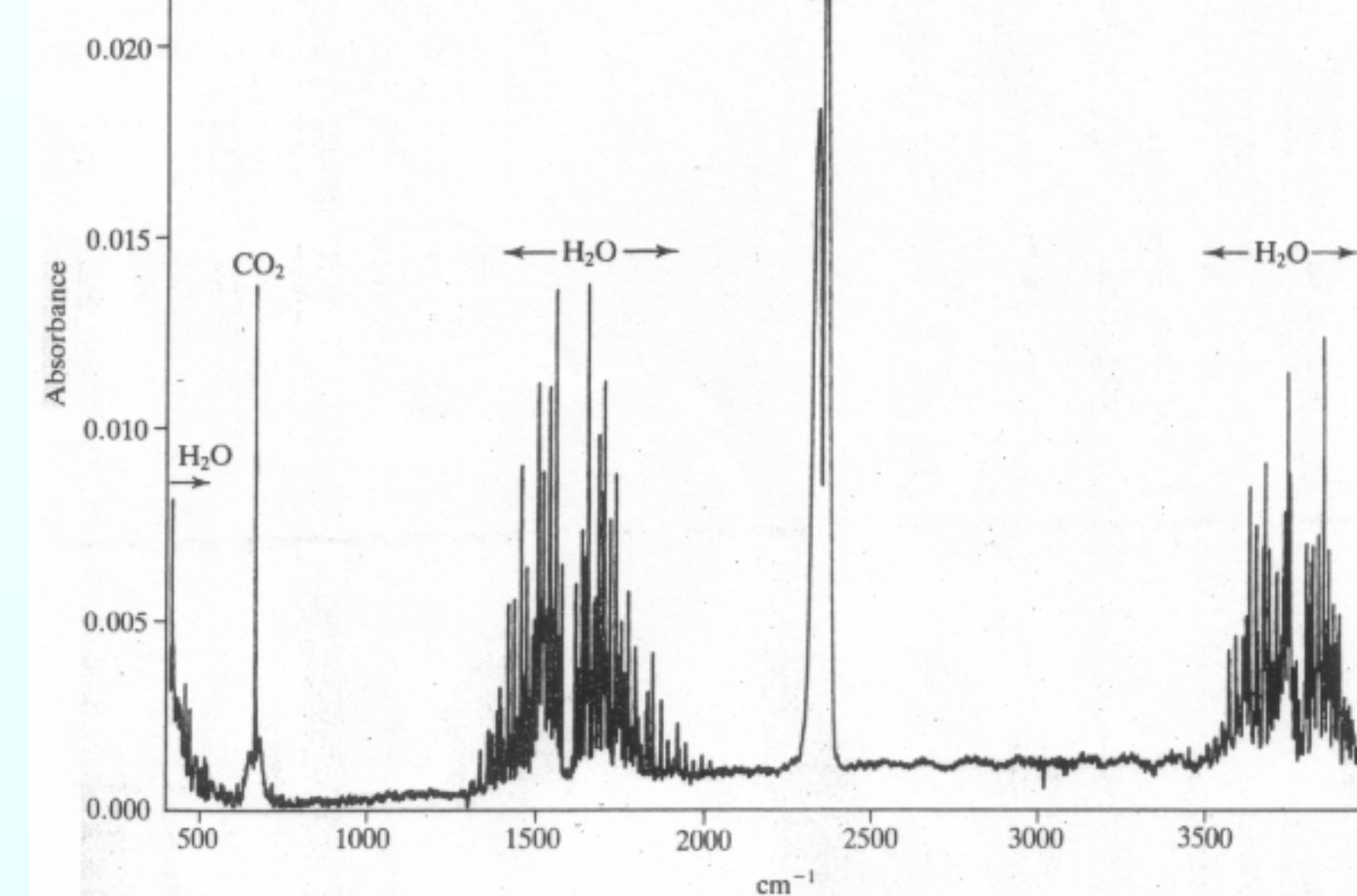
IR detectors used for TOC analysers can differ each other: one or more wavelength and single or double rays can be used, in the last case different reference gases are filled in a sealed reference cell or flow through an open cell. In order to avoid interferences from the above said IR absorbing gases, a selective gas-permeable membrane is situated in between the degradation and the detector chambers. In order to remove as much water as possible prior to introducing the gas stream into the IR analyser, air-cooled condensers are generally used.

Fig. 2, Infra Red (IR) spectrum of Carbon Dioxide (CO_2) in humid atmosphere, the absence of interference from water vapour can be evidenced.

Conductivity Detector

Even if completely aspecific, conductivimeter based detectors are widely used as simple and quite sensitive. They are especially used, coupled to the UV oxidation method, in the on-line analysis of high purity waters where the content of the interferent ionic species is very low.

Specific conductance is itself an important water quality index because it gives a good idea of the water salinity. Really, the conductivity in water is a measure of the ion-facilitated electron flow through it, it strongly depends on pH and temperature that influence all the solution equilibria. Some gases, most notably carbon dioxide, readily dissolve in water and interact to form ions, which predictably affect conductivity as well as pH.

Water conductivity must be measured accurately using calibrated instrumentation. The instrument must have a minimum resolution of 0.1 mS/cm on the lowest range.

For water having a conductivity below 1.0 mS/cm, a "flow through" cell may function better.

It is also opportune to use, as reference solution, high purity water with a known TOC level not higher than 0.25 mg/L.

CO₂ Electrode Detector

In the recent years, intense investigation has been undertaken on the TiO_2-assisted photochemical mineralization of organic substances by UV radiation, either with the semiconductor catalyst in suspension or immobilised on a solid support. The use of TiO_2 suspensions in the photocatalytic treatment of water sample can be coupled to a TOC determination by a CO_2 electrode. The sample is acidified so that all the inorganic carbon (bicarbonate and carbonate) present in the sample, that could interfere as generating CO_2, is eliminated and eventually measured as TIC, if the acidifying is performed during the flowing of the sample in the instrument but in absence of irradiation. The sample which flows into a stirred (to maintain the titanium dioxide in suspension) cell is irradiated by UV light in order to oxidise the organic carbon to CO_2; then it passes through a measuring cell containing a gas membrane electrode as detector.

The CO_2 electrode is not a conventional ion selective electrode (ISE) but can be better classified as selective gas-membrane electrode. Its functioning is based on the pH measure, by an internal glass electrode, of the inner solution; the carbon dioxide passing from the test to the inner solution through the selective membrane, due to its acidic nature, allows a pH change that can be related to its concentration.

A special care has to be paid in the choice of the pH buffer: it must not contain organic carbon so, all organic acid have to be avoided, a pH value no lower than 4 must be ensured during all the process (oxidation and measure) in order to avoid production of carbonate and bicarbonate.

The reproducibility of the measurements by the CO_2 electrode resulted to be ±2%. Potential electrode interferences can arise from the presence in the matrix of volatile weak acids (HCOOH, CH_3COOH, SO_2, and NO_2). Electrode potentials are also influenced by water vapour due to the changes in temperature that can be provoked and, in turn, changes in the solubility of CO_2 and shift in the equilibrium of the involved acid-base reactions. The upper limit of detection in pure carbon dioxide solutions is $1 \cdot 10^{-2}$ M and, at the best the L.O.D over $5 \cdot 10^{-5}$ mg/L.

Fig. 3, Distribution diagram [4] of carbonate, bicarbonate and carbon dioxide as a function of pH, it needs to work, with the CO_2 electrode, at pH values lower than 4.5.

Other Detectors

The flame ionisation detector (FID) was one of the first detector used to measure TOC and as such was used to measure fairly high levels of TOC.

In the TOC analyser, the aqueous sample is first broken down to CO_2 by the use of acids and a heated catalyst; then the FID reduces CO_2 sample to methane (CH_4).

Coulometric analysis is a technique in which the amount of a substance is determined quantitatively by measuring the total amount of electricity required to deplete a solution of the substance. Carbon coulometry is useful for the determination of TC, TIC and TOC in samples where the measurable carbon level exceeds 10 µg.

TC and TOC sample analyses are performed by first accurately weighing a portion of the sample, about 10-20 mg into a small platinum boat. The boat is placed into a quartz ladle and introduced into the quartz combustion tube. The ladle sits in a cool zone of the combustion tube while the system is allowed to purge. The carrier gas used with this system is 99.99% pure oxygen. The sample is then introduced into the heated portion of the combustion tube, which is typically heated to 950°. Here the oxygen-rich atmosphere reacts with the carbon in the sample to form CO_2. The combustion tube contains barium chromate to ensure complete conversion of CO to CO_2 and metallic silver, which removes interfering halides. The gas is then passed through a water trap and magnesium perchlorate scrubber to remove any remaining water vapour. The carrier gas then flows to the detector cell where CO_2 is adsorbed and coulometrically titrated.

Colorimetric method uses a spectrophotometer to measure the colour of a water sample after the oxidation process. An acid is added to the water sample to eliminate the inorganic carbon, then persulphate is added in the presence of UV radiation to oxidise the organics matter. The produced CO_2 passes through a semipermeable membrane and is then dissolved into a buffered phenolphthalein solution; the colour change of this acid-base indicator, measured by the spectrophotometer, can be related to the the pH variation caused by the increasing concentration of carbon dioxide.

Conclusion

Articles and reviews available starting from 1970 [5,6] and up today [7], demonstrated a great interest in the analysis of TOC. An increasing attention is really turned to the measure of TOC as an important index to assess the water quality [8]. At present a precise law on this topic do not exists probably due to the involved very complex issue; on the contrary many guidelines, by internationally recognised organisms, are available.

In the present communication we present a collection of the actually available rules, treating the TOC measure, useful to deep the argument and to allow a rightly critical reading of the literature on this topic. The last reveals that, in between the mineralisation methods, the photoassisted degradation [9] is actually the most studied for both the remediation of waste waters and for the compartment of the TOC analyser devoted to the oxidation of the organic matter.

Reference

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