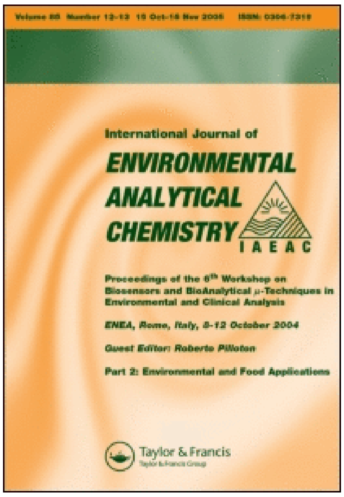

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Randon, G. , Dutang, M. , Rosset, R. , Caude, M. and Sassiat, P.(1985) 'An Industrial Analyzer by a Potentiometric Method for Total Organic Carbon in Water', International Journal of Environmental Analytical Chemistry, 20: 1, 1 — 12

To link to this Article: DOI: 10.1080/03067318508077042

URL: http://dx.doi.org/10.1080/03067318508077042

Intern. J. Environ. Anal. Chem. 1985, Vol. 20, pp. 1–12
0306-7319/85/2002-0001 $18.50/0

Printed in Great Britain

An Industrial Analyzer by a Potentiometric Method for Total Organic Carbon in Water[†]

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(*Received November 8, 1984*)

KEY WORDS: TOC determination, industrial analyzer, UV-peroxodisulfate oxidation, carbon dioxide indicating electrode, raw, town water and effluents monitoring.

This paper describes an industrial analyzer based on photochemical oxidation of organic substances present in water and on the measurement of released carbon dioxide by zero current potentiometry from a carbon dioxide sensitive electrode.

All apparatus functions are monitored by a microprocessor. A 100 ml nonfiltered water sample is taken at regular intervals and the inorganic carbon is eliminated by the addition of phosphoric acid and bubbling with compressed filtered air. Peroxodisulfate is introduced and an UV irradiation is carried out. The materials in contact with the sample in the irradiation cell are solely Pyrex glass, quartz and PTFE. Refrigeration of sample is retarded so that oxidation can take place at a temperature greater than the ambient. Oxidation efficiency is close to 100% even for aminocompounds which are more difficult to oxidize.

[†] Presented at the Fourteenth Annual Symposium on the analytical chemistry of pollutants, Barcelona, November 1984.

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Calibration is by the standard addition method and an automatic electrode response monitoring procedure with calibrated hydrogenocarbonate solutions has been perfected.

Analysis time is 30 minutes and the apparatus has a two-weeks autonomy. Measurement ranges are 0–20 ppm, 0–400 ppm, and 0–2000 ppm.

Results obtained in the 2–20 ppm range match laboratory measurements carried out with a DOHRMANN 80 analyzer.

INTRODUCTION

We described in a preceding article[1] the principles of measurement of total organic carbon (TOC) in natural waters and on the basis of which an industrial analyzer could be developed. It should be kept in mind that after the elimination of inorganic carbon by passage through an acid medium and bubbling of an inert gas, we have a strong oxidation of organic substances to carbon dioxide through the association of a chemical reagent, sodium peroxodisulfate $Na_2S_2O_8$ and an intense ultraviolet irradiation.

The CO_2 thus formed is measured by an indicating electrode whose potential varies, at 25°C, as follows:

$$E = \text{constant} + 0.059 \log |CO_2|$$

We obtain an oxidation yield of 95–100% for most organic compounds (hydrocarbons, chlorinated hydrocarbons, alcohols, phenols, amino acids, heterocycles, polyfunctional compounds). At the same time those compounds with an amino function are more difficult to oxidize but oxidation can be quantitative if the reagent reaction time is 10–20 minutes.

Accuracy on TOC is approximately 10% and minimum detection limit about 1 ppm carbon.

AUTOMATIC ANALYZER DESCRIPTION

The operation of the apparatus† is based on calibration by standard addition method. It therefore carries out sequential analyses.

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†The commercial name of the apparatus is "ANALYSEUR AUTOMATIQUE IGEA-COT". It is manufactured and sold by SEIT, 1020, rue des Bordes, Saran, BP 108, 45409 FLEURY-LES-AUBRAIS Cedex, France. Tel. (38) 43.03.03. Telex: 760848.

An integrated microprocessor triggers the automatic procedures of calibration and measurement, calculates the necessary parameters for determining concentration, and detects operational anomalies. The different steps in analysis are the following:

Sampling

The apparatus cleans itself and can work directly on natural water without pre-filtering so that the measured TOC corresponds not only to substances in solution but to the carbon present and also in (or on) particles in suspension. A large sample volume (100 ml) was intentionally chosen to be representative of the analyzed water.

Elimination of inorganic carbon

This is carried out by bubbling of compressed air at a 5 bar pressure with a flow rate of $2.5\,\mathrm{l/min^{-1}}$ during 5 minutes after the acidification of approximately 150 ml of analyzed water by an addition of 1 ml orthophosphoric acid $2\,\mathrm{mol.l^{-1}}$.

It has been shown that the carbon dioxide in the air used does not need to be eliminated (which could have been obtained by bubbling through a sodium hydroxide solution) because its solubility at pH near 2 was very low. Tests carried out on water with 50 ppm C in the form of a hydrogenocarbonate HCO_3^- showed that error in this case was less than 0.1 ppm.

At the same time, an activated charcoal filter retains all impurities that could interfere in TOC measurement (oil, organic matter, etc).

Inorganic carbon present in surface water (30 to 40 ppm) has been shown to be completely eliminated as it was present at less than 0.1 ppm in the TOC.

Photochemical oxidation

The decarbonated 100 ml of water is added with 1 ml of a 1 molar solution of sodium peroxodisulfate which is in large excess according to the carbon content in the analyzed water.

The irradiation chamber has a volume of exactly 100 ml so as to be completely filled by the sample. To avoid losses in CO_2 released during the reaction, it is made airtight to the atmosphere by means of a siphon on the cell overflow.

The UV irradiation lamp is a tube lamp type OSRAM HNS 15 W which allows a large contact surface with the solution to be analyzed. Its life time is approximately 6 months (the intensity then diminishes by 25% of its initial value).

The nature of the materials used (Pyrex glass, quartz, PTFE water-tight fittings) is such that there is no pollution of the sample by organic matter in the irradiation cell.

The UV lamp heats the solution to be oxidized. We have noted that it is preferable to use a timed refrigeration (the irradiation chamber has an external refrigerating envelope): an electrovalve controls circulation of the refrigerant just a few moments before the end of the reaction: oxidation is aided by an increase in temperature during most of the photochemical reaction. However, measurement with the CO_2 electrode is carried out at a constant temperature.

Figure 1 shows oxidation yield of a solution of 4-aminophenol with 20 ppm of carbon with continuous refrigeration and retarded refrigeration. It should be noted that the retarded refrigeration method leads to a much greater yield.

Transfer of the oxidized sample to the measurement cell

A 50 ml piston pump transfers the mineralized sample into the measurement cell. The first sample rinses the measurement cell with the water to be analyzed and the second completely empties the mineralization cell which is then ready to receive the following sample.

These operations are carefully carried out to avoid a loss of CO_2 during transfer. The piston is driven by compressed air at 5 bar pressure. Intake and discharge speeds are reduced by output limiters on the compressed air circuit.

CO_2 is measured in the measurement cell by an indicating electrode (ORION electrode model 95.02) with continuous stirring.

To avoid degassing the sample during measurement, the measurement cell is made airtight by a cover above the solution. A constant temperature is maintained by a circulation chamber which is supplied continuously by city water whose temperature is constant during the measurement time (temperature change in city water is very slow over time). This same water also supplies the refrigeration circuit of the photochemical reaction cell. Therefore all measurements are carried out at city water temperature.

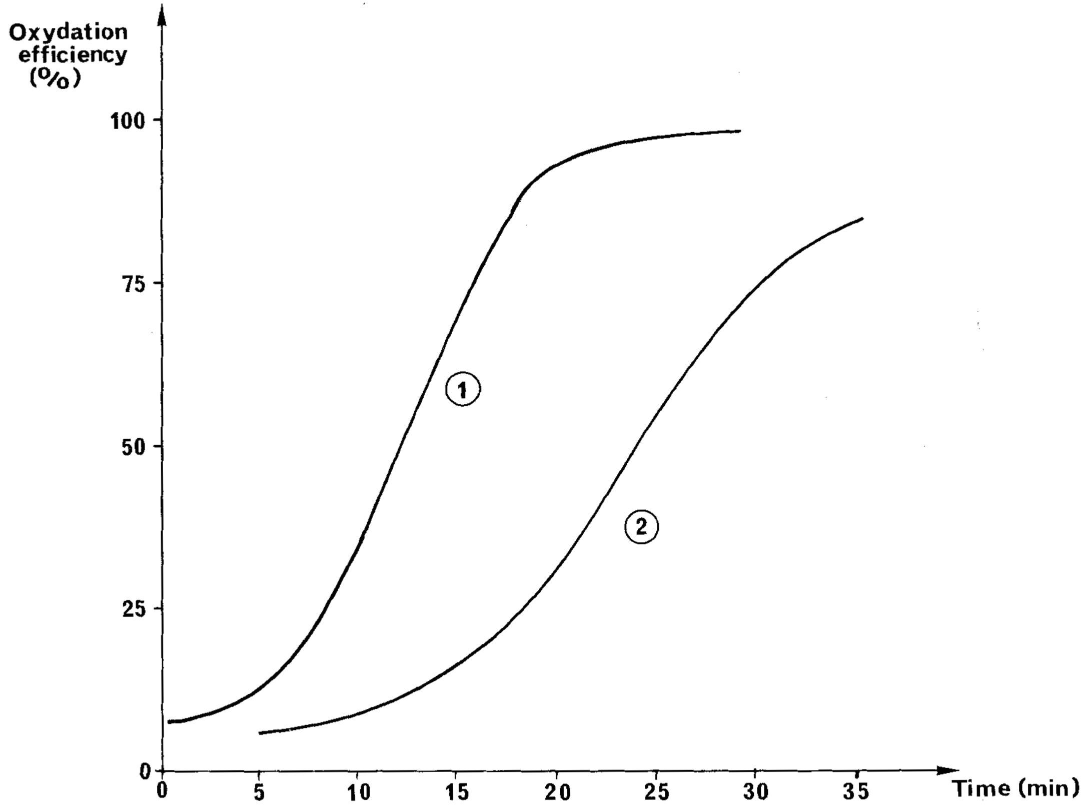

FIGURE 1 Influence of temperature on variation in oxidation yield of a solution of 4-aminophenol at 20 ppm of carbon versus time: (1) delayed refrigeration cell; (2) refrigerated cell.

Automatic calibration and monitoring of the apparatus

In the application of the standard addition method, possible fluctuations in the electrode's potential, whose theoretical value is 59 mV at 25°C, must be taken into account.

Automatic calibration consists of calculating at regular intervals the electrode's potential by carrying out two consecutive measurements on the two hydrogenocarbonate calibrating solutions in the distilled or demineralized water by passage through a cartridge of ion exchanging resins (contained in a storage reservoir with a capacity of 25 liters). It should be noted that these solutions do not pass through the UV irradiation cell and their organic carbon content is not imperative. These two solutions have concentrations in CO_2, C_1 and $2C_1$.

With E_1 and E_2 the potential values measured on these two solutions we have:

$$E_1 = E_0 + k \log C_1$$

$$E_2 = E_0 + k \log 2 C_1$$

thus:

$$k = \frac{E_2 - E_1}{\log 2} \quad \text{and} \quad E_0 = E_1 - k \log C_1$$

This calibration is automatically renewed every five measurement sequences.

Measurement of CO_2 concentration equal to C (potential E_3) is then carried out on the analysis water as well as a measurement with the addition of hydrogenocarbonate to the water so that its concentration in CO_2 has become $C + C_1$ (potential E_4).

Let us suppose that the electrode's potential has changed and that its value is k' ($\neq k$). We have:

$$E_3 = E_0 + k' \log C$$

$$E_4 = E_0 + k' \log (C + C_1)$$

We can state:

$$E_3 = E_0 + k \log \phi \; C$$

$$E_4 = E_0 + k \log \phi \; (C + C_1)$$

$k \log \phi$ measures the drift in the electrode's potential; if $\phi = 1$, $k \log \phi = 0$ and the drift is zero.

Thus:

$$\phi = \frac{1}{C_1}\left[\exp_{10}\left[\frac{E_4 - E_0}{k}\right] - \exp_{10}\left[\frac{E_3 - E_0}{k}\right]\right]$$

The measurement of E_1 and E_2 allows us to define k, and the measurement of E_3 and E_4 gives us ϕ. The constant monitoring of ϕ which would be equal to 1 if the electrode operated ideally, shows proper (or poor) analyzer operation. In this way the microprocessor judges the overall operation of the apparatus. When ϕ is less than 0.7 or greater than 1.3, the detected anomaly triggers a new calibration sequence. If ϕ is correct the measurement program continues normally. If ϕ is incorrect, the program is stopped at the end of the recalibration sequence and the anomaly is signalled. Intervention is then necessary to determine the apparatus's poor operation.

The concentration in CO_2 of the analyzed water is then:

$$C = \frac{1}{\phi} \exp_{10}\left[\frac{E_3 - E_0}{k}\right]$$

Analyzer description

The analyzer is contained in a metal chest with the dimensions 0.60 × 0.60 × 1.87 m in which are laid out the electronic and hydraulic parts necessary for automatic analysis (Fig. 2).

The core of the electronic part is a type 8085 8-bit microprocessor which triggers the different hydraulic organs during measurement and calibration sequences. It processes and uses results which are recorded on a printed strip. The controls of the hydraulic circuit can be manually operated through pushbuttons. The microprocessor can

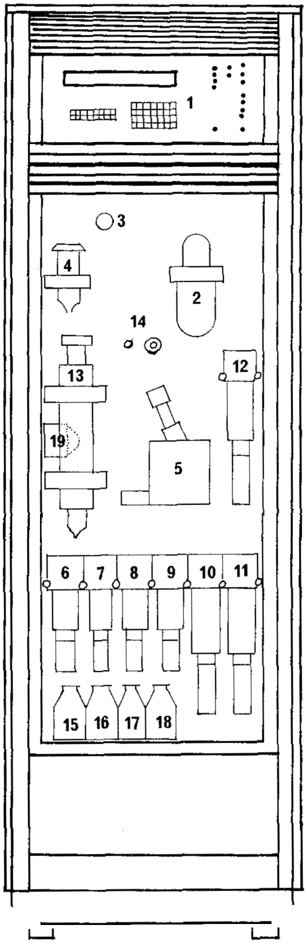

FIGURE 2. Diagram of the forward surface of the IGEA-COT total organic carbon automatic analyzer: (1) electronic rack; (2) air filter; (3) compressed air adjustment valve; (4) degassing tank; (5) measurement cell; (6) sodium peroxodisulfate solution doser; (7) phosphoric acid doser for elimination of organic carbon; (8) doser for phosphoric acid added to hydrogenocarbonate calibrating solutions used in measurement cell; (9) doser for sodium hydrogenocarbonate solution at 500 ppm C; (10) water doser after mineralization of organic carbon in the UV irradiation cell; (11) distilled water doser; (12) doser for supply of raw water to be analyzed; (13) UV irradiation cell; (14) connections for indicating electrode; (15) peroxodisulfate tank; (16) phosphoric acid tank for elimination of inorganic carbon; (17) phosphoric acid tank for measurement cell (added to hydrogenocarbonate calibrating solutions); (18) hydrogenocarbonate solution tank (standard addition method); (19) electrovalve for filling the UV irradiation cell.

be addressed by an alphanumeric keyboard and 40-characters display.

The hydraulic part includes the degassing tank for the elimination of mineral carbon, the thermostat, the volume dosers for the injection of reagents, the system for supplying the measurement cell in analysis water and in calibrated solutions (hydrogenocarbonate in distilled water corresponding to concentrations in CO_2, C_1 and $2C_1$) and the reagent tanks (Figure 3).

The UV irradiation cell is mounted on the forward surface.

The sample passes sequentially through the degassing tank, the UV irradiation oxidation cell and the measurement cell. To reduce analysis time, a cycle allows the mineralization of a sample while the preceding one is being analyzed (Figure 4).

Average measurement time is 30 minutes. An alarm system is included if thresholds are exceeded or if there is an anomaly in operation. The apparatus' autonomy is two weeks (supply of chemical reagents).

The normal range of measurement is 0–20 ppm C with a sensitivity of 1 ppm C. The apparatus may be adapted as follows:

—range 0–400 ppm with 20 ppm sensitivity
—range 0–2000 ppm with 100 ppm sensitivity

For the above adaptation the water sample is diluted with demineralized water obtained by passage through a cartridge of ion exchanging resins from BIOBLOCK Research (this quality of resin is necessary so as to have diluted water low in organic carbon) so that the TOC value is in the area of 0–20 ppm C.

RESULTS

Comparative analysis has been carried out with a DOHRMANN 80 analyzer (photochemical oxidation) on surface water and drinkable water produced by water treatment plants.

The results are gathered in Table I and show satisfactory results.

CONCLUSIONS

Photochemical oxidation followed by potentiometric measurement with a carbon dioxide indicating electrode has allowed us to develop

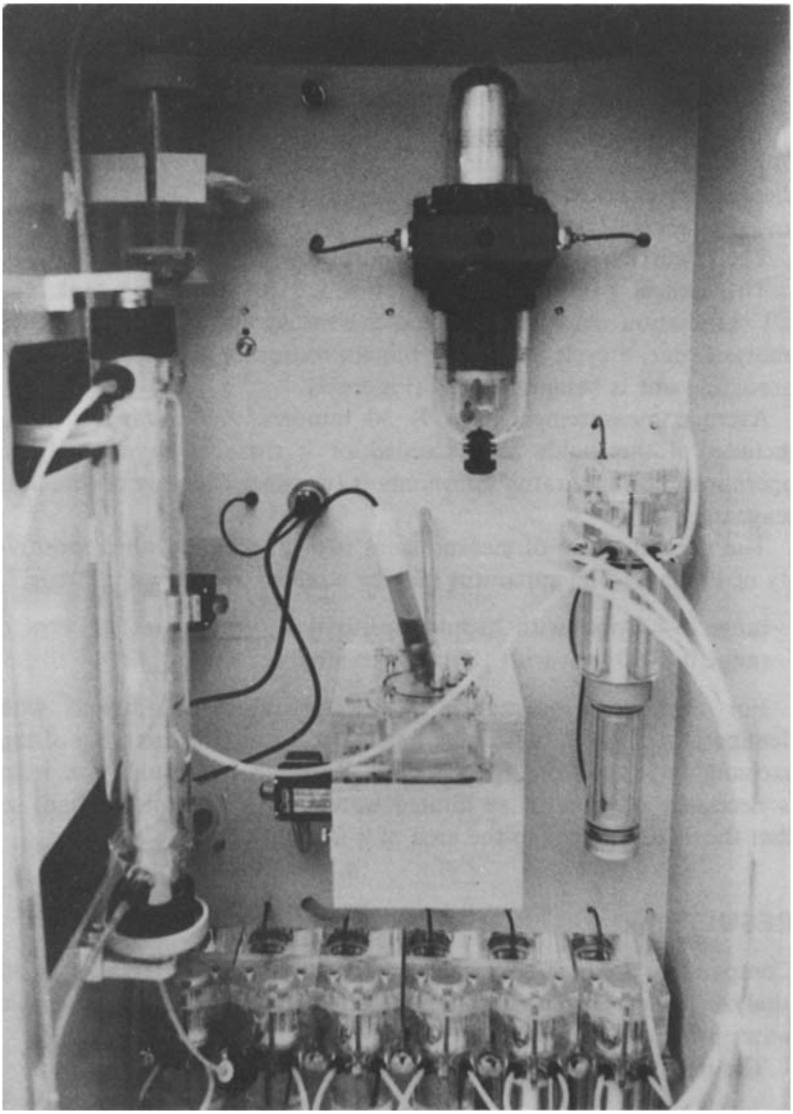

FIGURE 3 Photograph of the front of the apparatus with the measurement cell and its CO_2 indicating electrode. The UV irradiation lamp is on the left and below the volumetric dosers. The air filter is on the upper right and on the left the cell for the elimination of inorganic carbon dioxide.

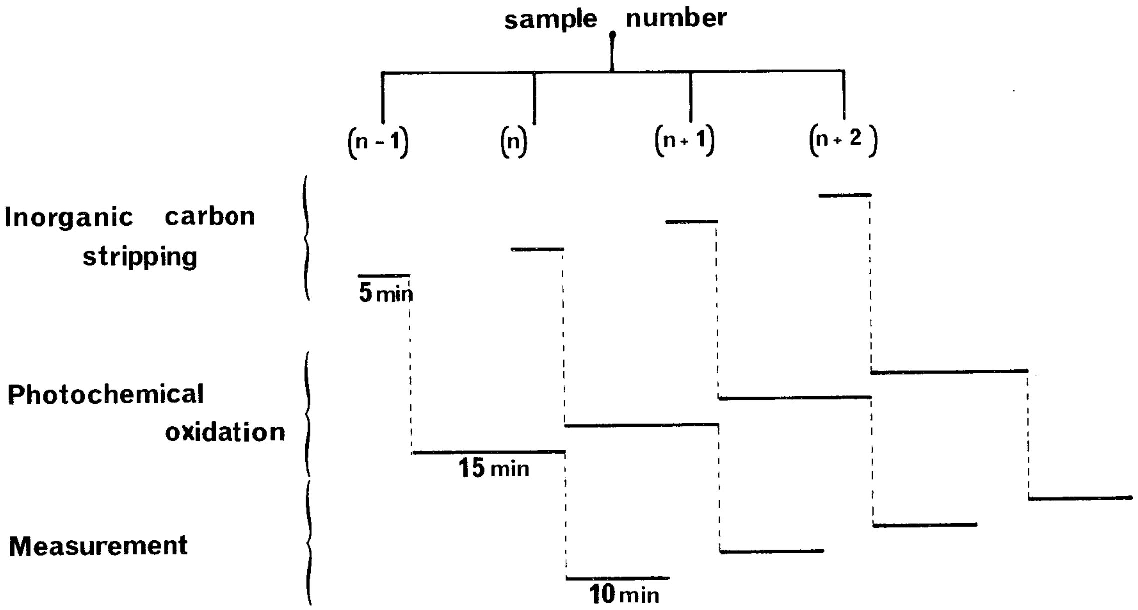

FIGURE 4 TOC measurement chronogram.

TABLE I
Comparison of results obtained on river water, effluents, and town water with the IGEA-COT automatic analyzer and the DOHRMANN 80 laboratory analyzer.

Source	Reference analysis	IGEA-COT Automatic analyzer
Orge (river)	5.6	7.0
Chantereine (river)	5.3	5.4
Orly Airport drainage channel	18.4	16.8
Orly Airport drainage channel (diluted 5 times)	4.0	3.2
Oise raw water at Méry-sur-Oise	6.3	5.7
Seine raw water at Choisy-le-Roi	3.7	4.0
Seine raw water at Neuilly-sur-Seine	4.6	4.6
Marne raw water at Noisy-le-Grand	3.0	3.6
Town water at Méry-sur-Oise	2.7	2.8
Town water at Choisy-le-Roi	2.4	2.3
Town water at Noisy-le-Grand	1.9	2.1

a TOC automatic industrial analyzer for water of highly varied nature.

It can be used to monitor river water upstream from a treatment plant or in places where pollution is feared (detection or alert) or in a treatment plant for the process of water purification. In the latter case it allows the determination of the efficiency of treatment. It can also be used by industry and water management agencies for monitoring effluents.

Reference

1. R. Rosset, M. Caude, P. Sassiat and M. Dutang, *Intern. J. Environ. Anal. Chem.* **13**, 19 (1982).