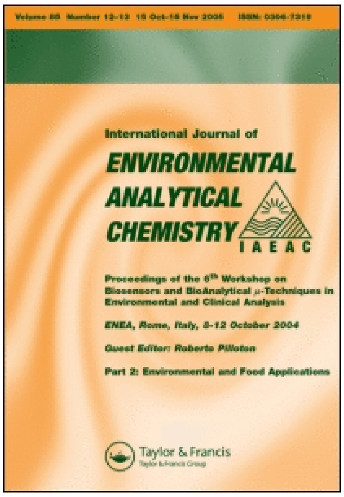

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Continuous Measurement of Total Organic Carbon in Water by a Potentiometric Method: An Industrial Analyser†

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The ultimate goal of our studies is the realisation of an industrial analyser for monitoring Total Organic Carbon (TOC) and detection of accidental pollution in rivers connected to treatment plants for drinking water. The apparatus must have high standards in robustness, easy servicing, low cost. On the other hand, sensitivity and accuracy are not as critical as for laboratory apparatus. An industrial apparatus has been devised operating by photo-chemical oxidation of organic matter (peroxodisulfate and UV light) and measurement of evolved carbon dioxide with a carbon dioxide sensitive electrode. Pumping system must not use plastic tubings as they pollute water; only Teflon® may be used. The pump is of the pneumatic amplifier type with a large-area gas driven actuating a small area liquid piston (Haskel pump type D). Reagents (phosphoric acid, peroxodisulfate) are introduced by simple pneumatic pumps (Varian). All tubings are in stainless steel or Teflon®. The cell volume is approximately 150 ml and the flow-rate of $2.0\,\mathrm{l.h^{-1}}$; so, the irradiation time is about 4–5 minutes. A series of chemicals representative of various families have been studied; hydrocarbons, chlorinated hydrocarbons, alcohols, phenols, amines, aminoacids, heterocyclic compounds, polyfunctional compounds. Oxidation efficiency is close to 95–100% unless for aminocompounds (diphenylamine: 50% at 13 ppm level; 4-aminophenol: 39% at 20 ppm level, etc.). Results indicate a sensitivity of 0.5 ppm, a response time of 15 minutes and an accuracy of 10%.

KEY WORDS: TOC determination, industrial analyser, UV-peroxodisulfate oxidation, carbon dioxide electrode.

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INTRODUCTION

Natural waters contain carbonaceous compounds to varying degrees. Inorganic carbon is present in the form of carbonates CO_3^{2-}, hydrogenocarbonates HCO_3^- and carbon dioxide CO_2. Organic carbon may be of natural or artificial origin and plays an important role in assessing the drinkability of water. "Normal" and "accidental" industrial discharge wastes very often contain various organic substances.

The expression "total organic carbon" (TOC) of a water applies to its carbon content due to organic compounds in suspension or in solution. Measurement of the TOC is of great practical importance because it serves to detect accidental pollution.

In the following pages we describe the development of an automatic system designed for continuous monitoring of the TOC of river water and alerting processing plants in case of accidental pollution.

We decided to develop a unit to meet a number of specific requirements characterizing a monitoring instrument and not an analytical instrument of the analytical research or control laboratory type. These requirements are the following.

1) These units will be installed upstream from the water intakes of treatment and purification plants and/or at the discharge points of industries considered the most pollutant, or at least incurring high pollution risks.

2) The instruments must be operational, with all the requirements that this implies from the standpoint of ruggedness, reliability, maintenance, price, operating costs, etc.

3) On the other hand, the problem is essentially one of detecting an abnormal increase in TOC. Consequently, the requirements are less stringent than for a laboratory instrument with respect to minimum detection limit and absolute accuracy of measurement.

This set of requirements eliminates most of the sophisticated instruments that have been described in the literature and/or marketed. This applies in particular to methods that use gas phase oxidation involving combustion tubes operating at elevated temperature (900 to 1000°C)

We directed our efforts towards a method usable at ambient temperature and combining:

oxidation in aqueous solution;

measurement of the carbon dioxide evolved by zero current potentiometry, using a CO_2 indicating electrode.

PRINCIPLES OF THE METHOD

Since inorganic carbon is previously eliminated by passage through an acid medium and bubbling of an inert gas, the organic substances are strongly oxidized to carbon dioxide through the combination of a chemical reagent, potassium peroxodisulphate $K_2S_2O_8$, and intense ultraviolet radiation. This method has been described in Ref. 1. It is assumed that under the action of peroxodisulphate and ultraviolet radiation, the water is decomposed with the formation of $OH^{\cdot}$ radicals which oxidize the organic matter. This occurs by two reactions:

$$S_2O_8^{2-}+2H_2O\xrightarrow{(UV)}2SO_4^{2-}+2H^{+}+2OH^{\cdot}$$

$$C_nH_m+(4n+m)OH^{\cdot}\rightarrow nCO_2+(2n+m)H_2O.$$

The CO_2 formed is measured by means of an indicating electrode (also called a "specific" electrode). The operation and characteristics of these electrodes have been described in great detail by M. Spoerri in her doctoral dissertation[2] and in Ref. 1. Briefly, it consists of a glass electrode immersed in a hydrogeno-carbonate solution containing sodium chloride, separated from the solution containing the carbon dioxide to be measured by an hydrophobic diaphragm (generally microporous PTFE). The dissolved carbon dioxide diffuses through the diaphragm into the internal electrolyte until the gas partial pressures on either side of the membrane are equalized. This results in a change in the electrolyte pH, which is measured by the glass electrode combined with an Ag/AgCl reference electrode.

The potential of the electrode varies (at 25°C) as follows:

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

The main drawback of this electrode is its relatively slow response to a variation in $pCO_2=-\log|CO_2|$. As the TOC *increases*, the response time ranges from 2 to 6 minutes. It is longer when the TOC *decreases*, up to 60 minutes. However, this is a minor disadvantage considering the requirements of the unit, because its job is to detect pollution and hence an increase in TOC.

CONSTRUCTION OF THE AUTOMATIC INSTRUMENT

Requirements concerning the various components

There are four requirements.

Choice of a pumping system. Problems raised by the chemical composition of the pipes. A simple pumping system could have involved the use of a multichannel peristaltic pump equipped with flexible hoses (Isoversinic, Tygon), and an instrument equipped with KEL-F® or polypropylene fittings.

We discovered that the use of a peristaltic pump operating by the crushing of flexible hoses causes significant pollution of the sample. In fact, pipes made of organic polymers are crushed by the pump rollers. As these pipes become worn, they release organic matter in suspension, and the latter is oxidized by the method employed ($S_2O_8^{2-}+UV$). Moreover, we observed that during the use of new pipes, the TOC rate was always very high, as the compounds detected were probably monomers or plasticizers which dissolve in the water to be tested. This occurrence was already pointed out by Takahashi[3] and Junk[4] who called it "sweating" of the flexible hoses. The organic matter content is rather high, and we estimated it between 10 to 20 ppm carbon, precluding any TOC measurement in a slightly polluted water.

Another problem concerns the pump delivery, which must be high considering the volume of the installation (150 ml). We selected a piston pump operating according to the Pascal principle (Haskel type D pump) which provided us with discharges up to 5 l/h.

Composition of the "pure" water used. The water used to prepare standard solutions must be rigorously free of organic matter, at the risk of distorting the calibrations. "Double softened" water obtained by passage through an ion exchange resin cartridge contains 2 to 10 ppm carbon and cannot be used. Water that is simply "distilled" in a standard apparatus is no better.

We employed water obtained by "evaporation" in a quartz unit (Quartex type PB.15) and stored in glass containers. This water has an organic carbon content less than 1 ppm (often around 0.6 to 0.8 ppm).

Choice of piping materials. Even is they are not used with a peristaltic pump, the "sweating" of flexible hoses causes pollution of the water samples that they convey. We replaced them with stainless steel tubes and, in order to secure a degree of assembly flexibility, by Teflon® tubes. The junctions between the lines and other parts of the assembly were provided by means of "Swagelok" stainless steel fittings and "Sovirel" glass and PTFE fittings. We made sure that the PTFE did not release any organic matter, by checking that the carbon content measured in water evaporated using the quartz unit was undetectable by the CO_2 electode, i.e. less than 0.5 ppm carbon.

Choice of the ultraviolet lamp and irradiation chamber. We selected germicidal lamps used in immersion (Osram type HNS 10 W). These lamps offer the advantage of being short (15 cm) of direct immersion in the reaction medium, making it possible to eliminate the cover around the lamp that causes a loss in energy.

Description of the assembly

The automatic unit developed in the laboratory (Figure 1) consists of a piston pump (Haskel) A making it possible to sample the test water continuously. Two gas pumps B and C (Varian) introduce the reagents (phosphoric acid solution and oxidizing peroxidisulphate solution). The mixture, which is produced by means of stainless steel tees, is introduced into irradiation chamber D. It is then cooled by passage through a gas cooler (air cooled) E and then sent to the measurement cell F.

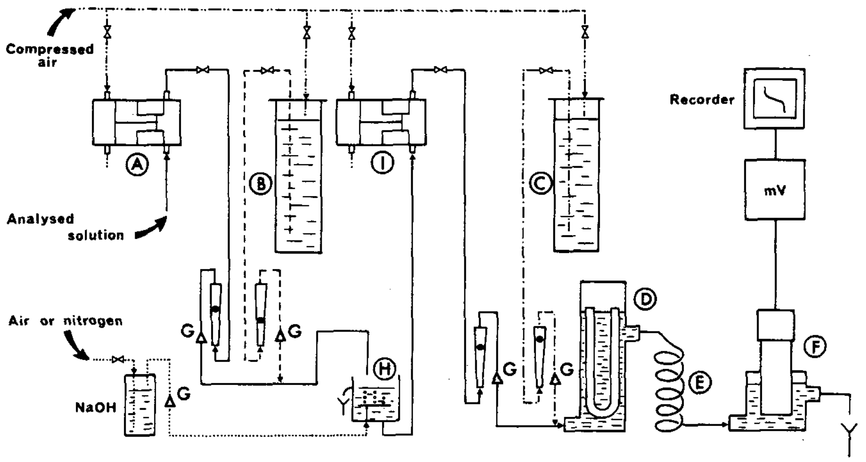

FIGURE 1 Diagram of automatic system designed to analyze natural waters: —··—··—··— compressed air; —·—·—·—·— peroxodisulphate solution; — — — — — phosphoric acid solution; ———— test solution; ······ air or nitrogen.

Stainless steel non-return valves G are mounted in the line after each pump to prevent any backflow from one into the other. The connecting pipes between these different accessories are of stainless steel and Teflon®, and connections are made by Swagelok type fittings.

Variations in the potential of the indicating electrode are measured using a Solea–Tacussel millivoltmeter and recorded versus time by means of a potentiometric recorder (Sefram).

To determine natural waters containing inorganic carbon, it is also necessary to eliminate the carbon dioxide originating in carbonates by the addition of an acid and the bubbling of nitrogen or decarbonated air. This means adding a degassing chamber H after acid addition and a second piston pump I to pick up the decarbonated solution.

ANALYSIS OF THE OXIDATION REACTION

Since this reaction combines a chemical reagent, peroxodisulphate with ultraviolet radiation, we have analyzed both factors.

Role of ultraviolet radiation

Figure 2 shows the potential variation of the indicating electrode as a function of time during the analysis of a potassium acid phthalate solution. Initially the analysis is performed without irradiation: the potential of the electrode remains constant and no oxidation occurs. In the second phase, the ultraviolet lamp is lit: the electrode potential rapidly increases and the oxidation reaction takes place. In a third phase, the ultraviolet lamp is extinguished, and the electrode potential decreases slightly. This shows that the use of ultraviolet radiation is indispensable to achieve the quantitative oxidation of organic substances present in natural waters.

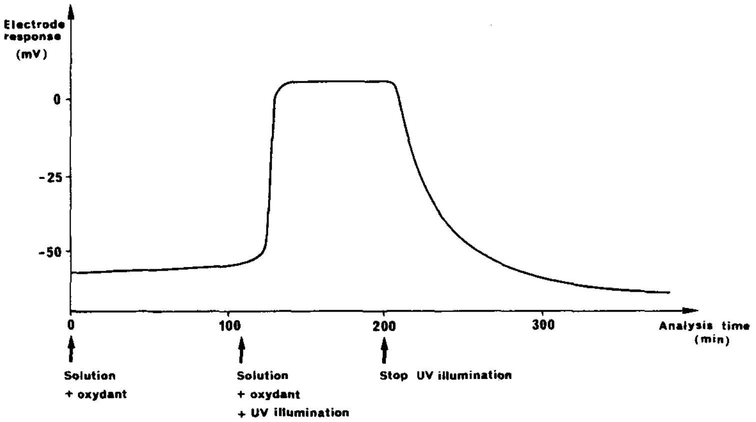

FIGURE 2 Analysis of a potassium acid phthalate solution (0.058 g·l^{-1}). Variation of response of the indicating electrode as a function of time. Effect of irradiation by ultraviolet rays.

Effect of the peroxodisulphate

Takahashi[1] showed that the oxidation yield of organic compounds to carbon dioxide becomes very low in the absence of peroxodisulphate, because the oxidation reaction that uses simple ultraviolet irradiation does not always produce carbon dioxide.

Effect of flow rate

With a flow input of around 2 l/h, the time of passage through the irradiation cell (volume 150 ml) is about 4 to 5 minutes. This interval is normally adequate to achieve quantitative oxidation of the organic compounds, except for those that contain an amino group. For these compounds, at a flow rate of 2 l/h, we observed that the electrode response does not correspond to the carbon content calculated by assuming an oxidation yield of 100%.

Figure 3 shows the variations in oxidation yield as a function of residence time in the reaction chamber for various compounds. It also shows that for a given flow rate, the oxidation yield is greater with decreasing organic compound concentration.

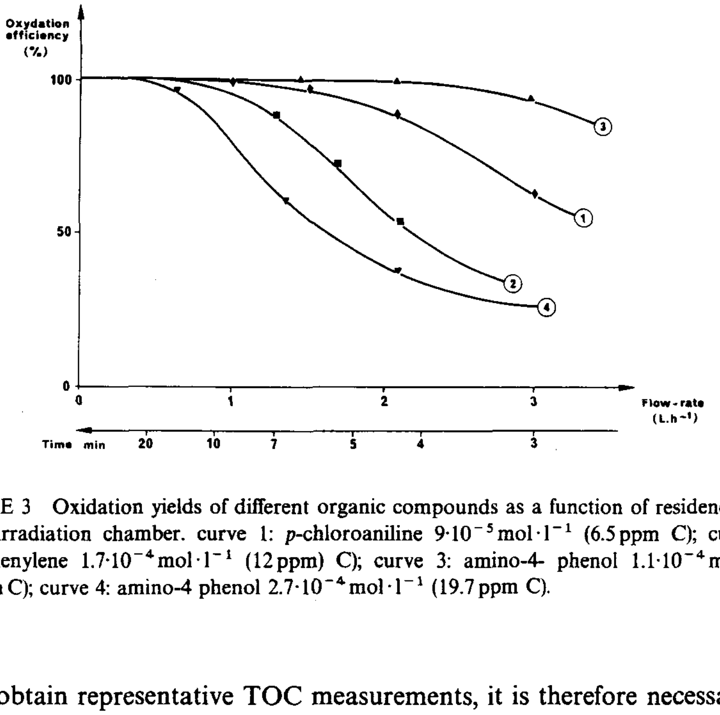

FIGURE 3 Oxidation yields of different organic compounds as a function of residence time in the irradiation chamber. curve 1: *p*-chloroaniline $9 \cdot 10^{-5} \mathrm{mol \cdot l^{-1}}$ (6.5 ppm C); curve 2: orthophenylene $1.7 \cdot 10^{-4} \mathrm{mol \cdot l^{-1}}$ (12 ppm) C); curve 3: amino-4- phenol $1.1 \cdot 10^{-4} \mathrm{mol \cdot l^{-1}}$ (7.9 ppm C); curve 4: amino-4 phenol $2.7 \cdot 10^{-4} \mathrm{mol \cdot l^{-1}}$ (19.7 ppm C).

To obtain representative TOC measurements, it is therefore necessary to increase the solution irradiation time. This can be achieved either by reducing the flow input (which lengthens analysis time), by mounting a second irradiation chamber in series (which also increases analysis time, but to a lesser extent), or by increasing the power of the ultraviolet lamp in the circuit.

Choice of optimal conditions

The foregoing results show that the optimal flow rate is 2000 ml·h^{-1}. As for the phosphoric acid and peroxodisulphate flow rates and concentrations, we selected them to correspond to considerable excess in comparison with the carbon contents in the water:

- 20 ml·h^{-1} of solution containing 1.5 mol·l^{-1} phosphoric acid;
- 20 ml·h^{-1} of solution containing 0.2 mol·l^{-1} peroxodisulphate.

RESULTS

The above system, used in the optimal conditions mentioned above, was employed on a series of solutions of organic substances considered to be representative of the various families of the main organic compounds liable to be encountered in river water pollution.

Table I lists the compounds selected and Table II shows the experimental results obtained. The TOC measured is determined from the calibration line obtained with the carbonate.

TABLE I
List of test compounds selected

Chemical family	Representative compound selected
hydrocarbon	iso-octane
chlorinated compound	methylene chloride
alcohol	methanol
phenol	dimethylphenol
amine	diphenylamine
	orthophenylenediamine
	trimethylamine
amino acid	glycine
nitrogen heterocycle	pyridine
polyfunctional compound	chloro-4 aniline
	amino-4 phenol

Yields marked with an asterisk correspond to amino compounds, of which the oxidation yield is not quantitative in the experimental conditions selected.

Accuracy on the TOC is around 10 to 15%. This is essentially associated with the fact that the CO_2 indicating electrode has a stability of about ±2 mV.

TABLE II

Experimental results (input flow rate 2·l·h^{-1})

Compound	Theoretical TOC (ppm C)	Electrode response (mV)	Measured TOC (ppm C)	Oxidation yield (%)
iso-octane	2.3	−67 (±2)	2.5 (±0.2)	108 (100/116%)
	5.2	−48 (±2)	5.2 (±0.5)	100 (90/110%)
	11.7	−28 (±2)	11.0 (±1)	94 (85/103%)
	15.5	−20 (±2)	16.0 (±2)	103 (90/116%)
methylene chloride	0.6	−94	(0.9)	
	1.5	−80	1.4	93
	2.6	−68	2.3	88
	3.8	−55	3.6	95
	5.5	−48	5.2	95
	9.7	−31	10.5	108
	15.1	−24	13.2	87
methanol	2.0	−73	1.9	95
	5.1	−51	4.7	92
	14.0	−26	12.5	89
	21.5	−14	20.0	93
dimethylphenol	3.8	−58	3.4	89
	10.0	−34	9.0	90
diphenylamine	13.0	−42	6.5	50*
orthophenylene-diamine	3.0	−70	2.2	73*
	12.0	−45	6.0	50*
trimethylamine	2.0	−85	1.2	60*
	6.6	−67	2.5	42*
glycine	5.0	−50	4.9	98
pyridine	0.5	−94	(0.9)	
	1.0	−92	0.9	90
	1.9	−70	2.1	110
	3.0	−64	2.7	90
	3.1	−60	3.1	100
	7.0	−45	6.4	91
	10.0	−34	9.0	90
	20.0	−17	18.0	90
chloro-4 aniline	1.2	−85	1.2	100
	4.0	−57	3.7	93
	6.5	−44	6.0	92
amino-4 phenol	7.9	−38	7.5	95
	19.7	−37	7.8	39
coronene	1.0	−86	1.1	110

CONCLUSION

The automatic system that we have developed is designed to determine an increase in TOC with accuracy of about 10% and a minimum detection limit of about 1 ppm carbon.

The instrument operates at ambient temperature, uses a rugged simple gas pressure pump, stainless steel, PTFE or glass piping, and a potentiometric measurement method that guarantees good reliability. The instrument requires minimum maintenance.

The response time for an increase in TOC (detection of pollution) is 15 minutes. On the other hand, response time for return to a low TOC (end of pollution) is about 60 minutes, because it is slowed down by the exchange kinetics in the neighbourhood of the porous diaphragm of the electrode. Nevertheless, this response is also satisfactory, because it is, in any event, shorter than the time of passage of the pollution in the river water.

One problem remains, however, the case of organic compounds containing an amine function. In this case, the oxidation yield is less than 100%, and this is liable to lead to underestimation of the pollution. One answer is to introduce a second irradiation chamber in the circuit, offering the two-fold advantage of a closer approximation of the type of pollution (by measuring the TOC after each chamber, a difference between the two values obtained indicates the presence of organic compounds that are difficult to oxidize), and of maintaining the instrument in operation in case of the failure of one lamp.

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