



Photochemical Sensor for Total Organic Carbon Measurement

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Introduction

The analytical determination of the organic concentration (set of organic substances dissolved and/or in suspension that can be present in a water matrix) is always a problem more and more in evidence in the environmental chemistry.

The measurement of the total organic carbon (TOC) is currently recognised as the best method for evaluation of the organic content in water's samples [1]. In fact his determination is regulated by European normative, which defines the operating analysis methods.

His determination is used as evaluation parameter of water purity grade. Comparing it with other parameters like BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand), TOC measurement emerges for selectivity, sensibility and fast execution.

The official analytical method, used for the analysis of the total organic carbon, consists in direct determination of the amount of the organic substances, through the measurement of the CO₂ produced by oxidation of organic substances present in an aqueous matrix upon acidification of it.

According to the normatives and guidelines at present in force [2] a new instrument (Fig. 1) has been planned for the measurement of the TOC. It is based on a photocatalytic process for the degradation of the organic substances and a gas permeable membrane electrode for the detection of the produced CO₂.

Main advantages of this device are the portability, the reproducibility and the low operative and maintenance costs.

Mark molecules

As tracing molecules, necessary for the development and the tuning of all the degradation parameters and measure of the instrument, a series of compounds having different characteristics between them, not only under the photodegradation point of view, but also on the basis of their different use and environmental impact, are chosen.

So, the possibility of analysing recalcitrant substances which resist to the degradation and tend to persist and accumulate in the environment (hydroquinone, dimethoate, aldicarb-sulfon, aspirin, parachlorophenol, citric acid, R-propranolol, acid blue 29 dye, D-glucose, atraton, atrazine) has been emphasised.

The chosen molecules differ from each other by presence of number of carbon atoms, by steric impediment and by presence of atoms which can interfere with the various components of the system (in particular electrode and catalyst), by the presence of oxygen atoms embedded in the molecules.

The choice was driven by the available bibliography that gave the possibility to compare results too. The characteristics of the used molecules are shown in tab. 1.

Commercial name	Parachlorophenol	D-Glucose	Acid Blue 29	Atraton Pestanal	Aspirin	Dimethoate Pestanal	Aldicarb sulfone	Hydroquinone	(R)-Propranolol	Citric acid	Atrazine Pestanal
Synonyms or IUPAC name	4-Chlorophenol, 4-Hydroxychlorobenzene, p-Chlorophenolic acid	Dextrosom (Glucosum) monohydricum, D-(+)-Glucose Monohydrate	2,7-Naphthalenedisulfonic acid, 4-amino-5-hydroxy-3-[(3-phenylazo)-disodium salt	2-Ethylamino-4-isopropylamino-6-methoxy-1,3,5-triazine	Acetylsalicylic Acid, ASA, 2-(Acetyloxy)benzoic acid, salicylic acid acetate	Phosphorodithioic acid O,O-dimethyl s-[2-(methylamino)-2-oxoethyl] ester, Roxion	1,4-Benzenediol, p-di-(methylamino) carbonyloxime Aldoxicarb	1,4-Benzenediol, p-di-Hydroxybenzene, Hydroquinol, Quinol	(R)-(+)-Propranolol Hydrochloride, 1-[(1-Methylethyl)amino]-3-(1-naphthalenyl)oxy)-2-propanol hydrochloride	Citric acid monohydrate, 2-Hydroxy-1,2,3-propanetricarboxylic acid	2-Chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine
C.A.S. number	106-48-9	14431-43-7	5850-35-1	1610-17-9	50-78-2	60-51-5	1646-88-4	123-31-9	318-98-9	77-92-9	1912-24-9
Molecular formula	C ₆ H ₅ ClO	C ₆ H ₁₄ O ₇	C ₂₂ H ₁₄ N ₆ Na ₂ O ₉ S ₂	C ₉ H ₁₇ N ₅ O	C ₉ H ₈ O ₄	C ₅ H ₁₂ N ₂ O ₃ PS ₂	C ₇ H ₁₄ N ₂ O ₄ S	C ₆ H ₆ O ₂	C ₁₆ H ₂₂ N ₂ O ₂ Cl	C ₆ H ₈ O ₇	C ₈ H ₁₄ ClN ₅
Formula weight	128.56	198.17	616.48	211.26	180.2	229.26	222.26	110.11	295.81	192.12	215.68
Melting point	43.2-43.7°	83°C	-	-	135°C	52-52.2°C	132-140°C	170-171°C	163-165°C	153°C	171-175°C
Absorbance (max) UV/Vis	228-284 nm (in water)	260-280 nm (in water)	602 nm (in water)	254 nm (in water)	229 nm (in H ₂ SO ₄) 277 nm (in CHCl ₃)	210 nm (in water)	211 nm (in water)	288 nm (in water)	214 nm (in water)	none	229 nm (in water)
Solubility in water	Sparingly	1.0 g/ml	20 mg/L	0.3%	< 1.0 g/L	very slightly	0.6%	70 g/L	50 g/L	59 g/L	70 mg/L
LD50 oral in rats	0.67 g/Kg	25 g/Kg	>200 mg/Kg	-	1.5 g/kg	250 mg/Kg	~1 mg/Kg	302 mg/Kg	320 mg/Kg	975 mg/Kg	850 mg/Kg
Occupational Exposure Limit*	0.5 mg/m ³ (sweden)	-	-	-	5.0 mg/m ³ (norway)	-	5 ppm	2 mg/m ³ (france)	-	-	5 mg/m ³ (norway)
Hazard Codes	Xn, N	F	-	Xn	Xn	Xn	T+	Xn, N	Xn	Xi	Xn, N
Use **	Used as an intermediate, a selective solvent and a denaturant	Used in food industries	Textile dye for wool, nylon and silk, non textile dye for leather, paper, casein	Pesticide, herbicide, weed control	Analgesic, anti-inflammatory and antipyretic	Systemic and contact insecticide for fruits and vegetables	Pesticide for agricultural	Reductant in Ullmann-type homocouplings	Drug, used as a beta-adrenergic blocking agent	Used in manufacture of citrates, silvering agent, medicine, food	Herbicide, used for season-long weed control in corn, sorghum and certain other crops

Tab. 1, characteristics of used molecules.

*The Registry of Toxic Effects of Chemical Substances **Centers for Disease Control and Prevention, 1600 Clifton Rd, Atlanta, GA 30333, USA

Description of method

The TOC is the combined total organic carbon present in compound dissolved and not dissolved. His determination allows to measure the real present organic carbon, after elimination of inorganic carbonates and other interfering.

The principal official methods for TOC analysis provide the direct determination of the CO₂ produced by the oxidation of the present organic substances in a aqueous matrix.

Also the technique used here is essentially based on the direct determination of the CO₂ produced by heterogeneous photocatalysis of a series of organic compounds containing a variable number of C atoms.

With this work, the realisation of a tool of measurement of the TOC which used the heterogeneous photocatalysis for the degradation of the organic substances and a gas permeable membrane electrode for the measurement of the produced CO₂, optimising a previous prototype [3] up to make him almost "portable", has tried.

The choice of the catalyst, of the lamps emission spectra and of the operating conditions, essential for a fast and efficient process, has been done by tests on some recalcitrant industrial dyes [4].

The chosen catalyst is the nanoparticled titanium dioxide (Degussa P25). The energy necessary to the break of the intramolecolari bonds and to the activation of the TiO₂ is provided by two light sources, one which reproduces the solar spectrum and one in the UV at 254nm.

Measurement apparatus

Sensor: gas permeable membrane electrode for the CO₂ (Crison, Mettler-Toledo). It is the sensor used for

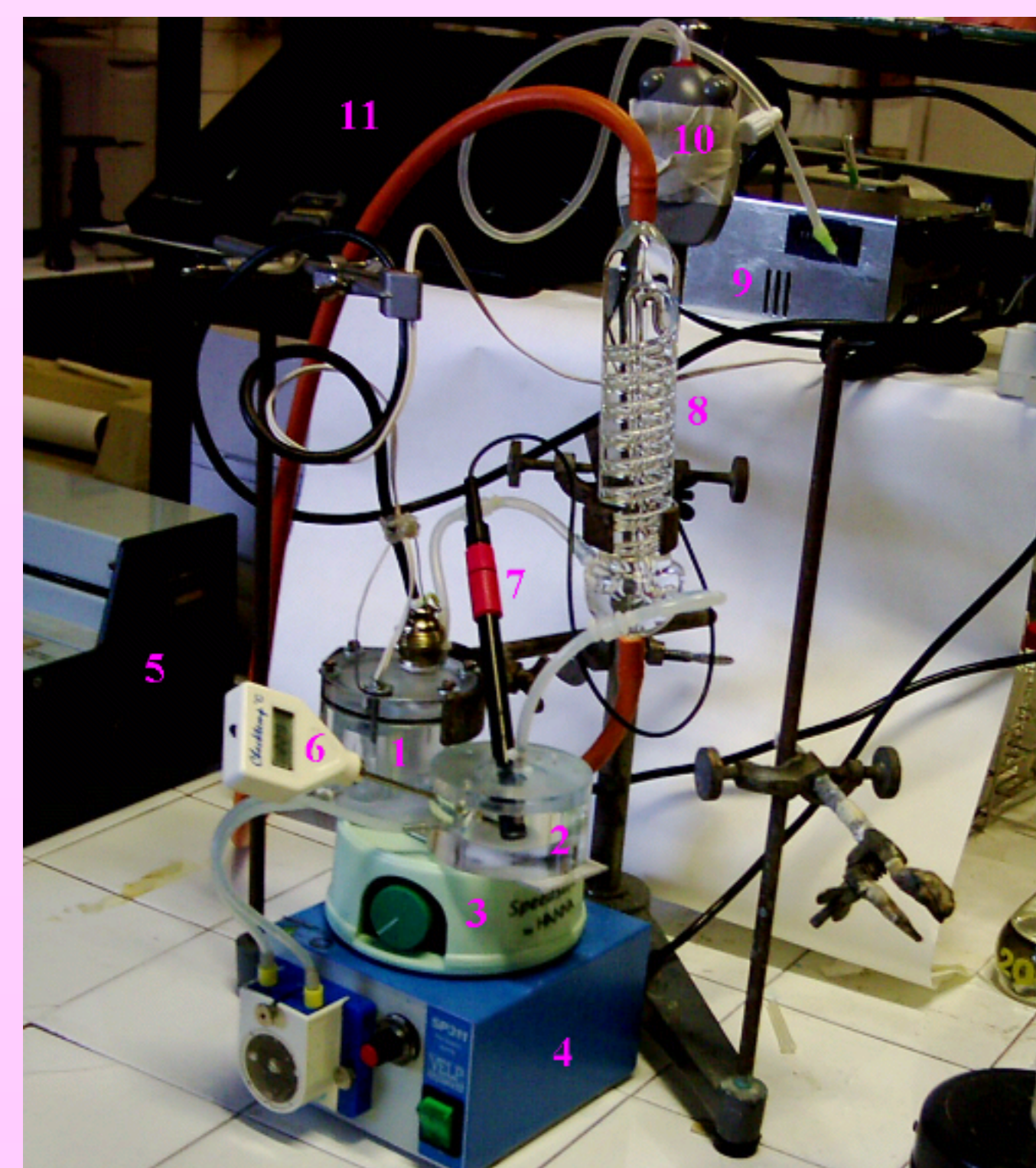


Fig. 1, Photocatalytic TOC measurement instrument. 1) reaction cell with two internal lamps UV-sunlight, 2) mesure cell with electrode, 3) magnetic stirrer, 4) peristaltic pump, 5) X-time chart recorder, 6) digital thermometer, 7) CO₂ gas permeable membrane electrode, 8) Dimroth condenser, 9) dual output power supply hand made, 10) membrane air pump, 11) pH-mV laboratory meter.

determination of the CO₂ produced by photodegradation of the samples. Periodically it is taken away from measure cell and calibrated in batch and flow.

Luminous source: it consists in two different lamps: a halogen bi-pin lamp with sunlight emulation (without UV-stop), model JC-Type, G4, 12V, 5W, GZ/GU 4, from Fluorimport S.r.l, Milan, Italy; an germicidal UV-C, Hg vapor GTL3 lamp, 60mm, 3W, E17, from Sankyo Denki Co.Ltd, Hiratsuka city, Japan with principal emission at 253.7 nm. The two lamps are completely dipped in the solution. All the power supply circuit has been planned and realised hand

made in house.

Catalyst: Titanium dioxide in the anatase form of the Degussa (surface area 50 m²/g, average diameter 20 nm particles). The catalyst has been chosen on the basis of the previous experiences of the group of research stretching the maximum efficiency.

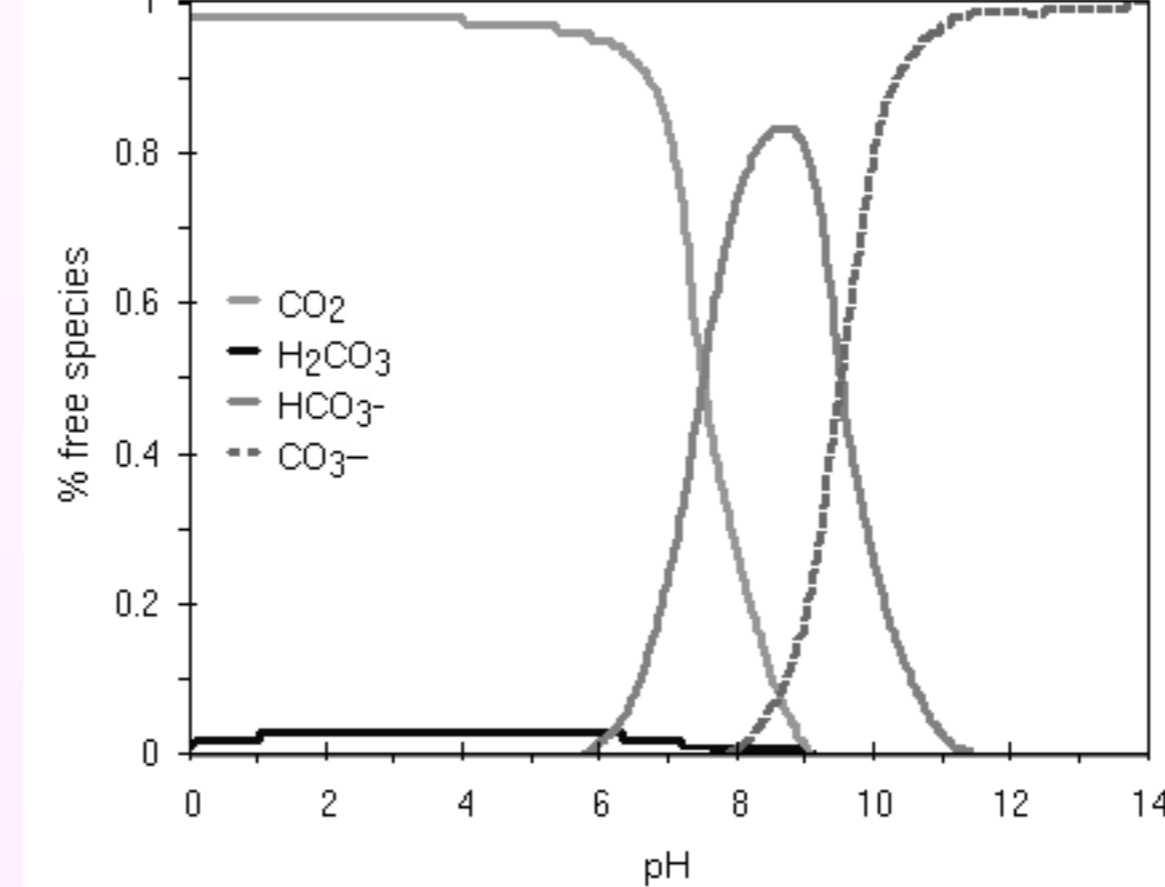


Fig. 2, Distribution diagram [5] of carbonate, bicarbonate and carbon dioxide as a function of pH, it highlights the need to work, with the CO₂ electrode, at pH values lower than 4.5.

Circulation system: it consist of a peristaltic pump (Velp Scientifica, model SP 311) and a magnetic stirrer (model HI 180, Hanna Instrument). They permit respectively to spread the analysed solution among the two cells and the refrigerant and assure the homogeneity of the catalyst's suspension in the system.

Oxygenation system: Membrane air pump for (Newair) aquariums. It permits to saturate the solution with filtrated air and consequently with oxygen, before or during the measurement.

Measurement of the photodegradation: the detection method for the concentration reduction of target molecules is an optical method carried out by a spectrophotometer UV/Vis (model Lambda 15, Perkin-Elmer). It permits to make parallel analysis and to make a comparison among data, obtained by photosensor or by bibliography.

Description of the method

The tool shown in photography 1, described in footnote, is used following an operating proceeding optimised with several previous prototypes.

The following steps can describe the operating procedure:

- wash the circuit using a large volume of bidistilled water and after with target solution (30 ml). This operation eliminates residue of previous target solution and makes couplement. After this the device must be empty and some TiO₂ have to be added. The TiO₂ must be present with a concentration of 1 g/L;
- pick up 85 ml of the target solution and, using a syringe, inject it in the cell containing the electrode;
- at the same time the peristaltic pump (in order to run the solution) and magnetic stirrer (in order to uniformly distribution of TiO₂) must be activate;
- by the means of another syringe, 9 ml of buffer phosphate (10% total volume) must be injected and the air is flow for 15 min;
- after turning off the air pump, wait for the stability of the system (8-10 min.) and check the mV value recorded by the electrode (V1). The gurgling phase eliminates CO₂ deriving from acidification of inorganic component (TIC);
- after adding a little hydroperoxide oxygen (about 1%), light sources must be turned on, keeping on the shaking, controlling flow and temperature;
- after standard time of 60 minutes (defined a priori for the photodegradation), the value recorded by the electrode (V2) in mV can be checked.

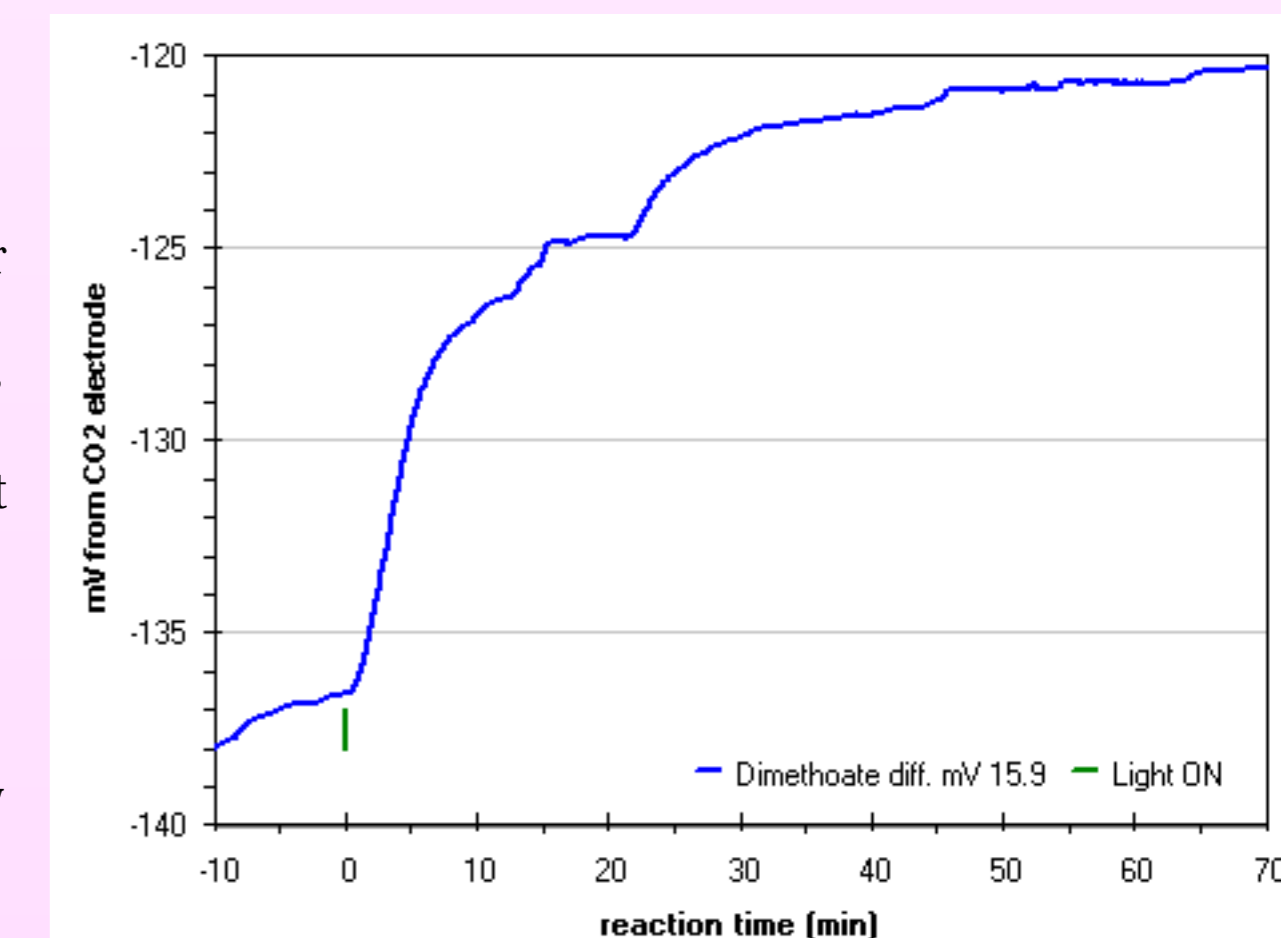


Fig. 3, Dimethoate 1.0 10⁻³ mol/L, mV-time chart of CO₂ electrode response. The green bar shows the lamps power on and the value of 15.9 mV is calculated after 60 minutes.

The variation of the potential recorded by the electrode (V2-V1) is proportional, in this case, to the degradation of compound analysed. Using this variation and by means of the periodic calibration curve of the CO₂ electrode, for the whole system, we can obtain the concentration (mol/L) of CO₂ produced by the decomposition of the sample. With some mathematical calculations of the CO₂ produced, we can obtain the value of the TOC (mg/L).

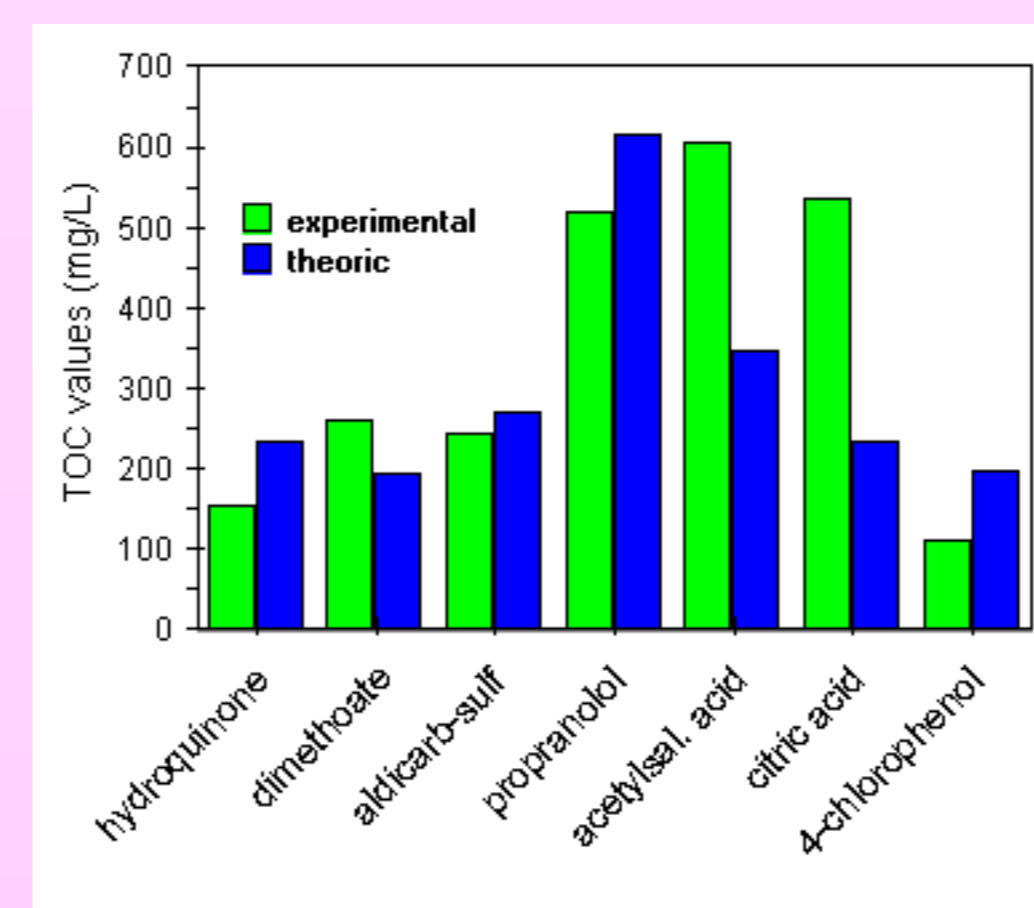


Fig. 4, TOC experimental and theoretical values, obtained for each compound, by means of the measurement of CO₂ produced by the photodegradation, and by the CO₂ calculated from carbon atom number present in the molecules.

improvement of the measurement experimental apparatus

Conclusion

A limit time of analysis has been fixed to better identify the various trends of the degradation, and also to evaluate the different recalcitrance of the compounds.

In Fig. 3 a typical time chart is shown, recording the potential of the CO₂ electrode vs the time, in this chart the trend of the degradation is obtained in only 60 minutes of recording.

The calculation, of the TOC starting from the CO₂ dissolved in solution and measured by the electrode, must consider many factors like the loss to the atmosphere, the presence of interfering, the kinetics of reaction, the reproducibility of the electrode, the overall response time, the different efficiency of the catalyst and so on.

The use of 11 target molecules, very different among theme, has allowed to consider the effects of all these factors.

TOC experimental and theoretical values are obtained, for each compound respectively, by means of the measurement of CO₂ produced by the photodegradation, and by the CO₂ calculated from carbon atoms number in the molecules.

The comparison (see Fig. 4) between these two values shows difference not higher of 40%; these good preliminary results urge to optimise the light sources and the reaction cell, to obtain a global

Reference

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