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A System for the Direct Determination of the Nonvolatile Organic Carbon, Dissolved Organic Carbon, and Inorganic Carbon in Water Samples through Inductively Coupled Plasma Atomic Emission Spectrometry

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A new system has been developed for the determination of total organic carbon (TOC) and inorganic carbon (IC) or total inorganic carbon (TIC) in waters. Only nonvolatile organic compounds can be detected through the present method. The system presented in this work is based on the measurement of the carbon atomic emission intensity in inductively coupled plasma atomic emission spectrometry (ICP-AES). This way, the organic matter does not undergo any preoxidation step. A semiautomatic accessory connected to the spectrometer separates the different carbon fractions (i.e., organic and inorganic). Because most of the solutions used in the present work did not contain suspended solid particles, the actual parameter that was determined was the dissolved organic carbon (DOC). The present system exhibits good sensitivities compared to those provided by conventional TOC and IC determination methods. The limits of detection obtained in the present work have been 0.07 and 0.0007 mg/L C in terms of TOC and IC, respectively. Furthermore, the system is able to handle high-salt-content solutions. This fact suggests that it would be possible to analyze seawater samples, avoiding some of the problems encountered with conventional methods, such as system blocking or interferences. The TOC and IC values found for natural samples are very close to those measured using conventional methods. The ICP-AES method has been successfully used in two interesting applications: (i) monitoring the efficiency of a water treatment plant and (ii) determining the contents of dissolved carbon dioxide, on one hand, and that of carbonate and bicarbonate, on the other, in the same sample.

In the field of water analysis, organic pollution can be expressed through the total carbon concentration (TC). It is possible to classify the different fractions of carbon according to the physical or chemical properties of the compounds present in the sample. Thus, one can find the so-called total organic carbon (TOC), which is defined as the amount of carbon covalently bonded as organic compounds present in the sample, and

inorganic carbon (IC), also known as total inorganic carbon (TIC), which corresponds to the sum of dissolved carbon dioxide, bicarbonate and carbonate.¹ TOC is a more suitable and direct expression of the organic pollutants than biochemical oxygen demand (BOD) or chemical oxygen demand (COD). This assessment is based on two main reasons: (i) TOC is directly correlated with the carbon concentration, irrespective of the oxidation state of the organic compounds, and (ii) theoretically, TOC is not influenced by the presence of some inorganic reducing agents. Typical TOC values in waters range from 0.001 to 50 mg/L C. The IC values, in turn, are dependent on the kind of sample, typical values lying around 25 mg/L C.²

In general terms, the methods used to determine TOC include four main steps:^{3–9} (i) a given volume of the sample is introduced into the system, and it is sometimes acidified; (ii) the sample is vaporized; (iii) the organic matter is completely oxidized to CO₂; and, (iv) this gaseous compound is driven toward a detector. TOC is finally calculated by means of a calibration graph. In these methods, called high-temperature combustion (HTC) methods, the oxidation of the carbon-containing species is normally carried out in vapor phase in the presence of a catalyst at temperatures ranging from 700 to 900 °C. Afterward, the generated carbon dioxide is determined by means of a nondispersive infrared analyzer.^{10–14} An ultrapure gas stream (e.g., oxygen,¹⁵ helium¹⁶)

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is used to drive the CO₂ toward the detector. Additional detection procedures include the use of an ion chromatograph¹⁵ or a hydrogen-flame ionization detector.¹⁶ With these modifications, the limits of detection (LOD) are reduced from 2 to 0.002 mg/L C.¹⁵

The main analytical problem in the TOC determination by HTC methods arises from the difficulty in controlling the temperature in the oxidation step, leading to deterioration in the precision of the results. Additional pitfalls of the HTC methods include¹⁷ (i) appearance of long memory effects, (ii) capillary blocking when working with high-salt-content solutions or with samples containing suspended solid matter, (iii) high background levels due to carbon release from the catalyst and some other parts of the system, (iv) sometimes the oxidation yield is too low (e.g., 82% for sulfathiazole), and (v) mechanical problems caused by the sudden expansion of the carrier gas stream as it enters the high-temperature column. For these reasons, alternative oxidation methods have been proposed, such as ultraviolet radiation^{11,18–20,33} or persulfate.^{4,15} In the first case, the sample is irradiated with far-ultraviolet radiation, which decomposes organic matter by means of a radical formation mechanism. Then the generated CO₂ is transported toward the detector using a carrier gas.

Dissolved organic carbon (DOC), defined as the concentration of organic carbon that is not retained on a filter with a 0.45- μ m pore size, is a parameter included within the TOC, and it is of great interest for the determination of the effectiveness of wastewater treatment procedures. Usually, natural waters show DOC values of up to several milligrams per liter. The radiative methods used for DOC^{4,6,14,18–20} and TOC are basically the same. The flow injection technique (FIA) methodology has also been applied to determine DOC.^{3,33} In this case, the sample is mixed on-line with persulfate and driven to an UV photoreactor. The hydroxyl radicals generated by persulfate are strong oxidants that transform the DOC into CO₂ that, at a rather high pH, remains dissolved as bicarbonate and carbonate. The following step is the acidification of the stream and the separation of the CO₂. Finally, this carbon dioxide is trapped by a phenolphthalein stream (pH = 8), the absorbance decrease at 552 nm being correlated with the DOC.

Sharp⁶ observed that the HTC methods provided better results than the chemical or radiative oxidation ones. In addition, the former methods are able to oxidize both volatile and nonvolatile organic compounds, whereas the procedure to determine non-volatile species through wet oxidation methods is more complicated. These reasons can partially account for the discrepancies in the results found using different methods. The radiation-based methods, in turn, do not need the use of any oxidant, but only trace amounts of a catalyst.

To determine the TOC, the IC must be removed from the sample. To this end, several methods have been proposed,^{21,34} the most common one being the addition of acid to the sample, to transform inorganic carbon into CO₂ and the use of a sparging/carrier gas stream to remove and drive the carbon dioxide toward the measurement zone.¹⁵ Alternatively, for the IC (or TIC) determination, the sample can be injected into a separated reaction chamber packed with phosphoric acid-coated quartz beads.²² IC can also be determined through the use of a semiautomated coulometric method. In this case, the calibration is performed from standards containing known concentrations of bicarbonate.²³

It is worthwhile to note that usually, the TOC value is obtained by subtracting the IC from the TC. Therefore, the precision might be significantly improved by determining these parameters in a direct fashion. The aim of the present work was, thus, to design and characterize a new system for the direct determination of TOC and IC (or TIC). We have used an Inductively Coupled Plasma Atomic Emission Spectrometer to measure the emission intensity at a carbon characteristic wavelength.

Plasma spectrometric techniques have been hardly applied to carbon determination.²⁴ In a recent paper, this technique was successfully used as a carbon detector for liquid chromatography.²⁵ However, to the authors' best knowledge, no attempt has been made to use the ICP-AES technique for the direct and simultaneous determination of TOC and IC. Few approaches have been found in the literature in which only DOC (or TOC) were obtained through ICP. Roehl and Hoffmann²⁶ deposited the sample onto a heated quartz tube filled with copper oxide and carried out a high-temperature oxidation of the organic matter. Then the resulting CO₂ was introduced into an ICP-AES. Emteryd et al.²⁷ coupled a FIA manifold to an ICP-AES system to obtain the TOC in natural waters after removing the IC. Bondarowicz²⁸ obtained the TOC in waters by carrying out a persulfate-assisted oxidation of the organic matter. The generated CO₂ was further introduced into the plasma. Owczkim et al.²⁹ used ICP-AES to determine dissolved organic carbon in soil solutions having carbon concentrations higher than 100 mg/L. However, our method can be applied to samples with lower carbon concentrations. Vogl and Heumann³⁰ used inductively coupled plasma mass spectrometry (ICPMS) for DOC determination in waters applying the isotopic dilution (ID) procedure. To this end, a ¹³C-enriched spike solution of benzoic acid was used. The cost of the analysis by applying this method was very high.

EXPERIMENTAL SECTION

Principle of Operation. The problems caused by a high temperature oxidation step could be solved by introducing directly the sample into an ICP. The plasma temperature in the analytical observation zone ranges from ~6000 to 8000 K.^{31,32} At these temperatures, any organic compound is fully dissociated, render-

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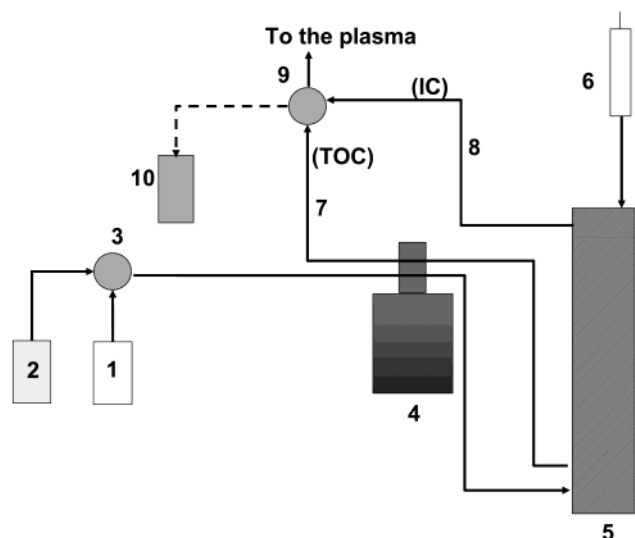


Figure 1. Scheme of the system developed in the present work: (1) sample reservoir, (2) hydrochloric acid reservoir, (3) valve, (4) peristaltic pump; (5) reactor, (6) rotameter, (7) liquid conduction, (8) gas conduction, (9) valve, and (10) waste reservoir.

Table 1. Instrumental Conditions of the Spectrometer

integration time	2.0 s
outer gas flow rate	14 L/min
intermediate gas flow rate	1.0 L/min
nebulizer gas flow rate	0.7 L/min
RF power	1.6 kW
IC carrier gas flow rate	0.4 L/min
viewing height above load coil	15 mm

ing their oxidation unnecessary. Thus, it is possible to measure the emission intensity at a carbon characteristic wavelength and correlate it with the carbon concentration in a sample of water. Because of this, the development of a FIA system to determine TOC and IC is significantly simplified.

Figure 1 shows an outline of the device developed in the present work to determine TOC and IC that can be easily adapted to a conventional ICP-AES spectrometer. The device includes the following components: (i) two polyethylene containers (1 and 2) for the sample and for a hydrochloric acid solution, respectively; (ii) two valves (type 50 model 5020, Rheodyne Incorporated, Cotati, CA) aimed to introduce either sample or acid solution into the stream (3, Figure 1) or to drive away the wastes (9, Figure 1); (iii) a peristaltic pump (4, Figure 1, Gilson Minipuls 3, Villiers Le Bel, France); (iv) a rotameter (6, Figure 1, series 2000, Tecfluid, San Just Desvern, Barcelona, Spain); (v) a reactor used to transform inorganic carbon into carbon dioxide (5, Figure 1); and (vi) an ICP-AES spectrometer Thermo Jarell Ash, Franklin, MA. Table 1 lists the instrumental conditions kept during the present study. The sample introduction system used was a conventional pneumatic concentric nebulizer (model AR-35-07-C2, Glass Expansion, Pty Australia) coupled to a cyclonic spray chamber (Glass Expansion, 40 cm³ inner volume).

Figure 2 shows a scheme of the reactor, which is the main component of the present device. It was made entirely of glass. Two capillary tubes were inserted down to the bottom of the sample volume, one corresponding to the argon line aimed to sparge the sample (1, Figure 2) and the other one used to evacuate

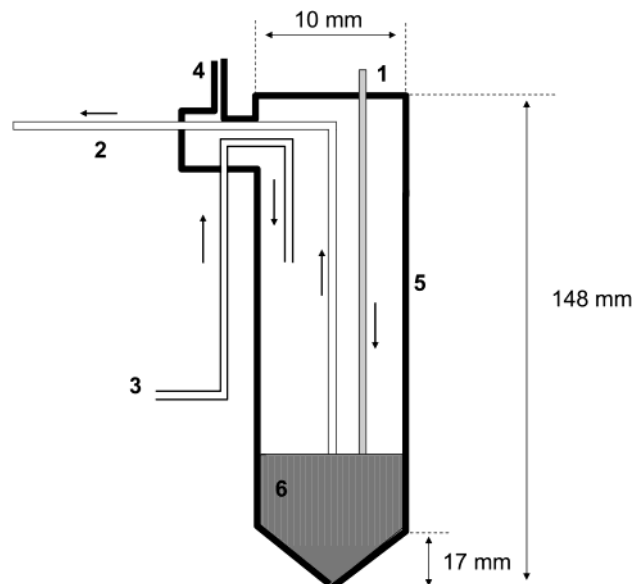


Figure 2. Scheme of the reactor used in the present work with its main dimensions: (1) argon sparging/carrier gas stream; (2) PTFE capillary to take the solutions away from the reactor; (3) PTFE capillary to introduce samples, hydrochloric acid, or washing solution inside the reactor; (4) vent to drive gaseous compounds toward the plasma; (5) reactor main body; and (6) sample.

the liquid from the reactor (2, Figure 2). Any liquid solution was introduced into the reactor by means of a capillary (3, Figure 2). Finally, an upper vent (4, Figure 2) was adapted at the top of the reactor in order to drive the vapor compounds toward the plasma. The inner volume of this reactor was ~16 cm³.

The operation mode of this system could be described as follows (see Figure 1): A given volume of sample was pumped into the reactor. Then, by modifying the position of valve 3, a volume of HCl solution was introduced into the reactor to transform the IC into CO₂. By opening the rotameter (6), the CO₂ was carried toward the plasma through capillary 8. The argon carrier gas flow rate was kept at 0.4 L/min. This argon stream emerged through the nebulizer central capillary and was introduced into the cyclonic spray chamber. Therefore, under these conditions, the total gas flow rate reaching the plasma center was 1.1 L/min. The emission intensity was registered by the ICP-AES spectrometer as a transient signal. In the present work, the peak height was correlated with the IC by means of a set of calibration standards prepared from sodium bicarbonate. At this moment, it should be pointed out that a sparging step might remove a fraction of the volatile organic carbon, thus giving rise to a lack of accuracy and precision; however, in most of the cases, the content of volatile organic compounds in natural samples is negligible compared to that of nonvolatile ones.

Once these steps were accomplished, the pump was switched on. Thus, the liquid sample was aspirated and introduced into the plasma through capillary 7 after having modified the position of valve 9. The solution was finally delivered to the nebulizer central capillary. In most of the experiments, the sample volume was high enough to reach a steady carbon signal instead of a transient one. In this case, the calibration standards were prepared from potassium hydrogen phthalate (KHP).

Before analyzing a new sample, a washing cycle was to be applied. A complete IC–TOC–washing cycle took ~5 min.

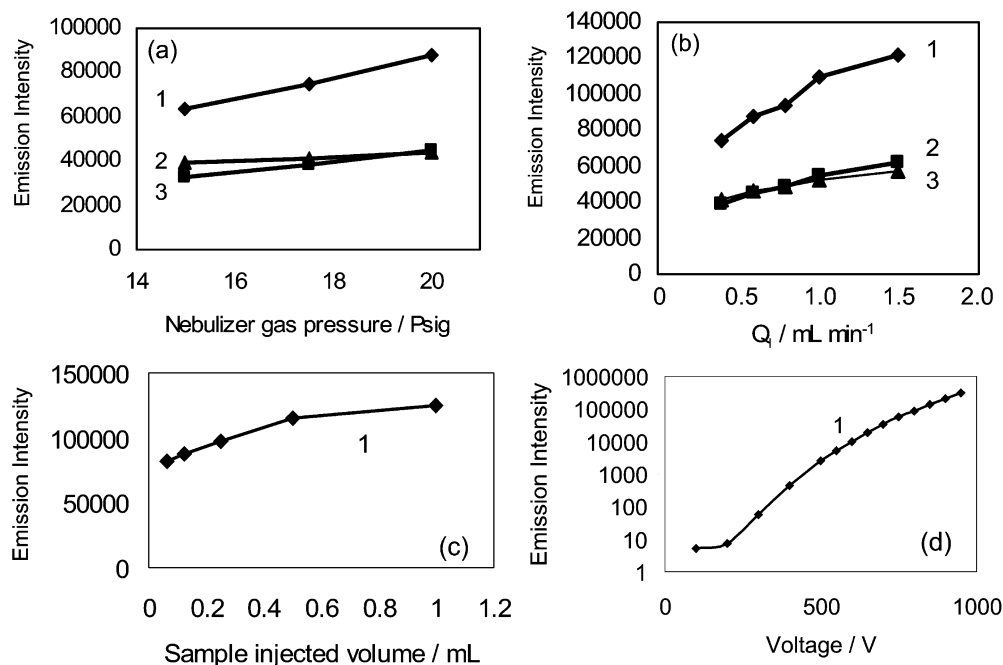


Figure 3. Emission intensity of a KHP solution (100 mg/L C) versus (a) nebulizer gas pressure, liquid flow rate = 0.5 mL/min; (b) liquid flow rate, nebulizer gas pressure = 20 psig; (c) sample injected volume, nebulizer gas pressure = 20 psig; liquid flow rate = 1.5 mL/min; (d) PMT applied voltage, nebulizer gas pressure = 20 psig; liquid flow rate = 1.5 mL/min. Wavelengths used: (1) 193.090 nm, (2) 165.700 nm, and (3) 247.856 nm.

An automated Shimadzu TOC V-SCN analyzer was used as a conventional reference apparatus. The operating conditions were as follows: sample injected volume, 50 μ L/min; combustion temperature, 680 $^{\circ}$ C; carrier gas, ultrahigh-purity air; and carrier gas flow rate, 150 mL/min.

Reagents. All of the reagents used in the present work were of analysis grade purity (Panreac, Spain). Stock solutions (1000 mg/L C) of nonvolatile organic compounds were prepared by weighing 174 mg of glucose, 294 mg of lactic acid, 250 mg of acetic acid, 525 mg of oxalic acid, 172 mg of EDTA, 510 mg of urea, 172 mg of nicotinic acid, and 269 mg of citric acid and dissolving them with distilled water to a final volume of 100 mL. Less concentrated standards were prepared by an appropriate dilution of the stock solutions. To prepare the 1000 mg/L C stock solutions corresponding to volatile compounds, 134 mg of phenol, 187 mg of butan-1-ol, 145 mg tetrahydrofuran (THF), 217 mg of methyl isobutyl ketone (MIBK), 266 mg of methanol, and 199 mg of ethanol were weighed and dissolved into 100 mL of distilled water.

RESULTS AND DISCUSSION

Preliminary Studies and Optimization of the Variables.

The emission spectrum of carbon was registered when just distilled water was introduced into the plasma. The background was readily high. However, a carbon signal was easily observed at the working wavelength. This signal corresponded to minor amounts of CO₂ carried by the solution, the argon stream, and the surrounding atmosphere. Therefore, to obtain accurate results, the contribution of these sources of carbon to the final signal had to be considered when determining TOC. For that reason, when only TOC was obtained, the solution was first sparged with an argon stream. However, since in the present work, attention was focused on the determination of both TOC and IC, the acidification-sparging step eliminated partially this source of error.

Several optimization experiments were performed using a 100 mg/L C solution prepared from KHP. Figure 3 plots the carbon emission intensity versus the nebulization variables, that is, the nebulizer gas applied pressure (3a) and the liquid flow rate (3b), the sample injected volume (3c), and the photomultiplier tube (PMT) applied voltage (3d). Figure 3a and b shows that the carbon emission intensity increased as both the nebulizer gas applied pressure and the liquid flow rate went up. These results can be explained in terms of mass of carbon transported to the plasma. On one hand, for a given liquid flow rate, the mass of carbon reaching the plasma was higher as the nebulizer gas flow rate (i.e., applied pressure) was increased, because the aerosols generated by the nebulizer were finer at high than at low gas flow rates. On the other hand, at a given gas flow rate, the mass of carbon entering the plasma was also higher as the total mass of sample nebulized (i.e., liquid flow rate) was increased. All these studies were carried out at three different emission wavelengths. From Figure 3a and b, it emerged that the best results (i.e., highest sensitivities) were obtained at 193.090 nm.

Concerning the sample injected volume (Figure 3c), the signal obtained using 65 μ L was just 33% lower than that obtained using 1 mL. With this method, it was thus possible to achieve good sensitivities with a minimum sample consumption volume. Similar trends have been found in the determination of IC. For the sake of comparison, coulometric methods used for IC determination require sample volumes as high as 50–100 mL to carry out a single measurement,² whereas spectrophotometric flow injection methods reduce the volume of sample required down to about 500 μ L.²

The spectrometer used in the present work was equipped with a photomultiplier tube (PMT) for the UV region. Figure 3d shows that the emission intensity sharply increased with the voltage

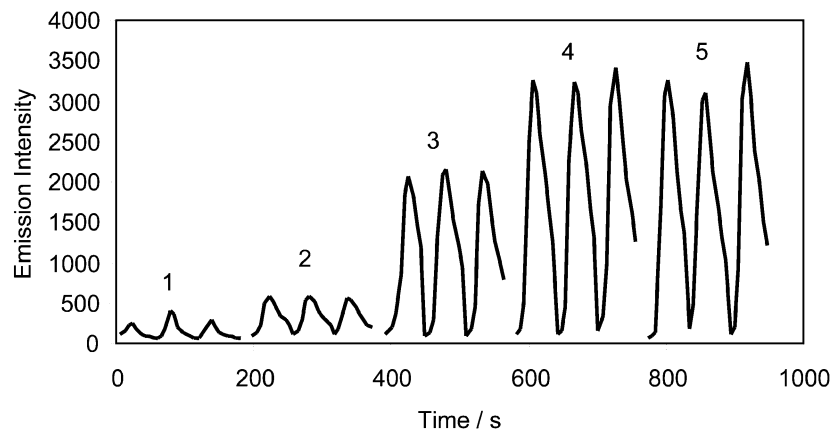


Figure 4. Transient signals obtained when determining IC for several HCl concentrations: (1) 0, (2) 0.001, (3) 0.005, (4) 0.01, and (5) 1 mol/L. IC, 20 mg/L; PMT voltage, 408 V; wavelength, 193.090 nm.

applied to the PMT dynodes, the most significant increase being observed above 200 V. To prevent rapid tube deterioration, the voltage was automatically set by the instrument.

For IC determination, HCl concentration plays a very important role. Figure 4 shows that the peak height increased with HCl concentration up to 0.01 mol/L. Above this value, the peak height remained constant. Therefore, the use of an HCl concentration lower than 0.01 mol/L resulted in an inefficient conversion of carbonate and bicarbonate into CO_2 . According to the data presented in Figure 4, it would be necessary to use 5×10^{-5} mol of HCl per mg of inorganic carbon present in the sample. As can be seen in Figure 4, the transient signals were recorded for a period of 55–60 s. Note that under the conditions tested in the present work, the time required for a complete release of the CO_2 generated from the solution was ~ 2 min. When determining the TOC after the IC, the sparging time was set at 3 min so as to ensure a complete release of the CO_2 .

Studies with Several Organic Nonvolatile and Volatile Compounds and Matrix Effects. The emission signal obtained in ICP-AES must be related to the carbon content of the sample irrespective of the organic compound. Figure 5 shows the relative emission intensity, that is, emission signal divided by carbon concentration, for a set of 8 organic nonvolatile compounds (5a) and 5 volatile organic compounds (5b). In the case of nonvolatile organics, this parameter was found to be similar for all the compounds tested, the values ranging from 94 (glucose) to 106% (EDTA). Therefore, this method could be considered suitable for the determination of the nonvolatile fraction of the organic carbon (NVOC), even in the case of “difficult” compounds, such as nicotinic acid, for which other FIA methods have been reported to supply low recoveries.^{33,34}

However, if the sample contains volatile organic compounds (Figure 5b), the relative signals appeared to be very different from one another. This difference arose from the sample introduction step. As has been previously mentioned, a pneumatic nebulizer was coupled to a cyclonic spray chamber. It has been demonstrated that volatile compounds are more efficiently transported to the plasma than nonvolatile ones. As a result, the mass of carbon injected into the plasma was higher for the former, thus leading to higher emission signals. Among other factors, the vapor

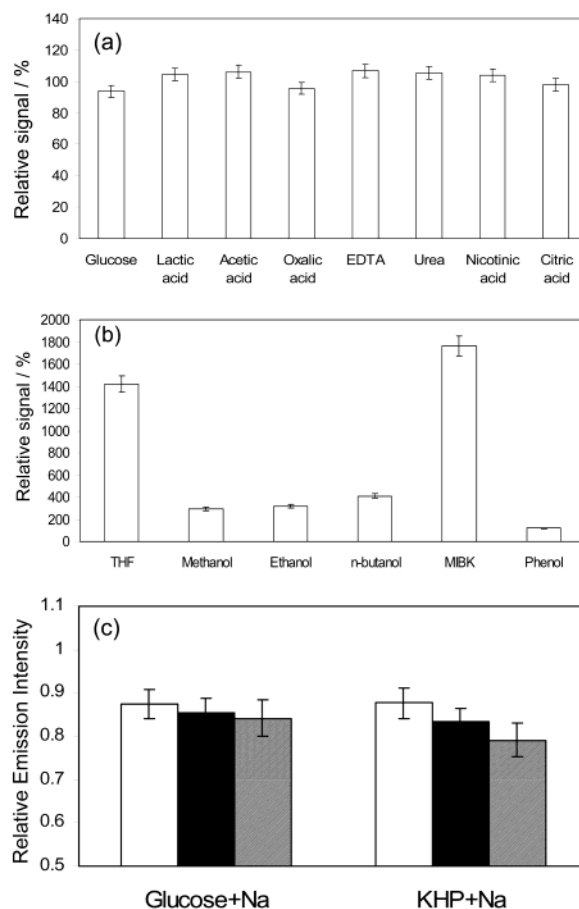


Figure 5. Relative emission signal, that is, carbon emission signal/carbon concentration $\times 100$, for several solutions prepared from nonvolatile organic compounds (a) and volatile organic compounds (b) and relative intensity, that is, carbon emission intensity in the presence of sodium, 5000 mg/L, divided by carbon emission intensity in absence of sodium for three different wavelengths (c). White bars, 193.090 nm; black bars, 165.700 nm; gray bars, 247.856 nm; PMT voltage, 800 V. In all cases, the TOC was 100 mg/L C.

pressure and number of carbon atoms appeared to be responsible for the relative order in sensitivities showed in Figure 5b as a function of the volatile compound. Concerning the vapor pressure, it has been observed that for compounds having the same number of carbon atoms, the higher the vapor pressure, the greater the relative intensity. Thus, at 25 °C, the vapor pressure for THF is

(34) Huber, S. A.; Frimmel, F. H. *Anal. Chem.* **1991**, 63, 2122–2130.

10 times higher than that for butan-1-ol (i.e., 158 and 15.7 mmHg, respectively).³⁵ As a result, in aerosol phase, THF evaporates faster than butan-1-ol does, thus enhancing the emission signal. Concerning the number of carbon atoms, from Figure 5b, it became evident that the relative signal followed the order methanol < ethanol < butan-1-ol < MIBK. This trend was found despite the higher vapor pressure for methanol or ethanol than that for the remaining volatile compounds. The results shown in Figure 5b meant that when analyzing samples with volatile compounds, the calibration procedure should be performed by using the same organic compound as that present in the sample. This fact made the determination of VOC with this method challenging. Fortunately, in most natural samples, the content of volatile organic compounds is usually negligible versus that of nonvolatile ones.¹⁷

High concentrations of easily ionized elements (EIE) are often found in some kind of samples. This matrix causes several unwanted effects in ICP-AES.³⁶ Among them we can find (i) the deterioration in the nebulization process due to partial or total nebulizer blocking, (ii) the modification in the mass of analyte transported toward the plasma, (iii) the blocking of the injector tube and the quick deterioration of the torch, and (iv) the modification in the local and global plasma excitation characteristics. To extend this method to the analysis of seawater samples, solutions of glucose and KHP containing sodium at a concentration of 5000 mg/L were analyzed. The results were compared with those found for plain water solutions of the same compounds. Figure 5c shows the carbon signal in the presence of sodium divided by that in its absence for these two organic compounds at three different carbon emission wavelengths. A value of 1 in this parameter meant no matrix effects. It appears that the relative signals were always lower than 1, the drop being somewhat smaller at 193.090 nm. In the best of the cases, the signal dropped by just 10% in the presence of sodium.

Analytical Figures of Merit. When measuring the TOC using the present method, a steady-state signal was obtained. Hence, the precision of the method used was very good (i.e., about 1–10% RSD). When determining the IC (or TIC), the precision of the method is a very important parameter for some applications. Thus, Stoll et al.² found that to monitor the changes in this parameter in marine waters, a precision of $\pm 2 \mu\text{M}$ was required. In the present work, IC was measured as a transient signal. When determining IC, the relative standard deviation calculated from 11 peaks was 2.2%. Therefore, the precision achieved in the present work was $\sim 35 \mu\text{M}$. This value was of the same order as those found using other flow injection methods.³⁷

A maximum sample throughput of ~ 50 determinations/h (TOC or IC) could be calculated taking into account that a washing cycle of ~ 15 s would be applied between two consecutive samples. The reported sample throughput was ~ 3 – 8 determinations/h for coulometric methods² and ~ 45 determinations/h for FIA–spectrophotometric methods.^{2,33}

The dynamic range for the determination of TOC in waters has been tested. Table 2 shows the results of the calibration lines obtained at the two most sensitive wavelengths tested. Eight

Table 2. Calibration Equations and Test of Lack of Fit for the Two Most Sensitive Wavelengths Tested

wavelength (nm)	equation	R^2	F_{calc}
193.090	TOC (mg/L) = 5063 + 129 I_{emission}	0.9990	1.90 ^a
247.856	TOC (mg/L) = 1278 + 31 I_{emission}	0.9995	0.44 ^a
193.090	IC (mg/L) = 1180 + 139 I_{emission}	0.9959	1.65 ^b

^a For a 95% confidence level. $F_{\text{tabulated}} = 3.13$. ^b For a 95% confidence level. $F_{\text{tabulated}} = 4.37$.

standards of known carbon concentration contained between 10 and 1000 mg/L C prepared from potassium hydrogen phthalate were analyzed. Despite the high correlation coefficient (i.e., $R > 0.999$), the linear model obtained was validated by means of an analysis of variance of the regression. The lack of fit test described by Massart et al.³⁸ was then applied. As can be seen, at 95% significance level, the linear model was adequate to describe the variation of the emission signal with the carbon content of the sample (i.e., $F_{\text{calculated}} < F_{\text{tabulated}}$). These conclusions were reached even for concentrations as high as 1000 mg/L C and using a single sample volume. In contrast, other conventional methods described in the literature³⁹ require modification of the sample volume in order to enlarge the dynamic range. In those instances, the dynamic linear range could be extended from 10 μg of C/L to 5 mg/L C.

Concerning the IC determination, Table 2 also shows the corresponding equation for the calibration line found at the most sensitive wavelength. Again, the lack of fit test revealed the validity of the linear model. The linearity was good at least up to 250 mg/L C. If we compare the intensities measured for IC with those found for TOC, it can be seen that similar signals were obtained. This fact was attributed to the different PMT applied voltage (see Figure 3.e).

The limits of detection have been calculated according to the $3s_b$ criterion, where s_b corresponds to the standard deviation obtained from 20 replicates of the background signal. The LOD found for TOC determinations was 0.07 mg/L C. This value was lower than that reported for the method based on the use of an ICPMS system (i.e., 0.3 mg/L) in combination with the isotopic dilution procedure³⁰ and similar to²⁹ or even lower²⁶ than that reported by other methods using ICP-AES, though in ref 29, the LOD were calculated according to the $2s_b$ criterion. The LOD found for IC determination were 2 orders of magnitude lower than those obtained for TOC. This difference can be attributed to the fact that when measuring TOC, just 2–3% of the carbon delivered to the nebulizer reached the plasma. However, because CO_2 was generated when determining IC, it was removed from the sample and introduced into the spray chamber, this percentage could be considered to be close to 100%.

Edwards et al.³³ reported LOD values between 0.09 and 0.22 mg/L C for FIA methods based on the oxidation of the organic matter by persulfate, the dynamic range going from 0.1 to 2 mg/L

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Table 3. TOC and IC Results for Different Natural and Synthetic Samples

sample	sample ID	TOC (mg/L)		IC (mg/L)	
		ICP-AES method	conventional TOC method	ICP-AES method	conventional IC method
river surface water	1	12 ± 1	13 ± 1		
river groundwater	2	17.6 ± 2	10.8 ± 4		
urban waste	3	45 ± 4	38 ± 4		
urban waste	4	73.4 ± 3	75.7 ± 8		
urban waste	5	52 ± 6	74.8 ± 8		
urban waste	6	93 ± 6	76.2 ± 8		
urban waste	7	111 ± 10	148 ± 20		
spiked seawater ^a	8	135 ± 14	184 ± 20		
synthetic sample ^b	9	208 ± 15	238 ± 20		
synthetic sample ^c	10	282 ± 12	356 ± 40		
water with surfactant ^d	11	1330 ± 20	1170 ± 100		
drinking water	12			24.0 ± 0.2	24 ± 1
drinking water	13			19.0 ± 0.2	22 ± 1

^a Actual TOC value, 150 mg/L C. ^b Actual TOC value, 200 mg/L C. ^c Actual TOC value, 300 mg/L C. ^d Actual TOC value, 1300 mg/L C.

C. A very sensitive FIA approach based on the oxidation of the organic matter assisted by UV radiation afforded limits of detection as low as 1.5 µg C/L, but its dynamic range was extended up to only 3 mg/L C.³⁴ On comparing these methods with the high-temperature-combustion (HTC) ones, it appeared that the former were less expensive and afforded better sensitivities. Nevertheless, they exhibited lower recoveries and worse precision and were more sensitive to the matrix effects caused by sodium chloride.

Analysis of Real Samples. The method described in the present work has been applied to the analysis of water samples. The results obtained have been compared against those found using a method in which the organic matter was oxidized within a high-temperature column and the CO₂ produced was determined by means of an IR analyzer. Table 3 summarizes the results found for two river surface (no. 1) and ground (no. 2) water samples and five samples corresponding to urban wastes (nos. 3–7). Samples were preserved inside glass flasks, and 0.01 mL of concentrated sulfuric acid was added to 50 mL of sample. It can be concluded that within the limits of error, for this wide variety of samples, there was a good agreement among the results provided by both methods.

Besides these samples, four synthetic samples were prepared: a spiked seawater sample (no. 8); two samples having a simple matrix similar to that found in the case of natural surface and groundwaters (nos. 9, 10); and another one containing sodium dodecyl sulfate (no. 11) at a level above the micelle critical concentration. No significant differences were found between the two methods tested. These results indicated that the present method was also suitable for the analysis of seawater samples, surface and groundwaters, and waters containing detergents.

The speciation of inorganic carbon was carried out on two samples. The IC fraction present as dissolved CO₂ was determined by sparging the solution, after placing it inside the reactor, with an argon stream. The concentration of CO₂ in the samples was ~15 mg/L C. Afterward, a given volume of a 0.01 mol/L HCl solution was added to the sample so that the carbonate and bicarbonate were turned into CO₂. By sparging the sample again, it was possible to obtain the carbon signal corresponding to these species. Table 3 summarizes the results found for two different bottled drinking water samples in terms of carbon content provided by the carbonate and bicarbonate species (nos 12 and

13). A reference method based on sample titration with HCl in the presence of methyl orange as indicator was used for comparison. It can be seen that the results found for both methods were in good agreement.

CONCLUSIONS

The present work has demonstrated the reliability of a new system for the determination of TOC (or DOC) and IC (or TIC) in waters of different nature. According to the analytical figures of merit provided by the method, it can be applied to drinking as well as wastewater samples.³³

On comparing the present ICP-AES method with that based on the use of an ICPMS, similar results were found in terms of limits of detection for TOC determination. Furthermore, two additional advantages of the ICP-AES method could be invoked. First, there is less interference by sodium, thus making it easier to analyze seawater samples with an optical rather than with a mass spectrometer. Second, the lower cost of an ICP-AES system makes the present method very attractive for assessing the organic pollution level of a water sample, provided the large number of ICP-AES apparatus existing worldwide (i.e., on the order of 40 000).

In conclusion, it can be stated that by using easy chemical speciation methods, it is possible to obtain very valuable parameters from the point of view of environmental analysis. Concerning the future trends, it seems possible to develop a single system able to give us information about TOC, DOC, IC, and heavy metal contents in waters of different nature by using ICP-AES as a detection technique. These studies, which are being currently carried out in our laboratories, would greatly expand the field of application of ICP-AES to the environmental analysis.

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