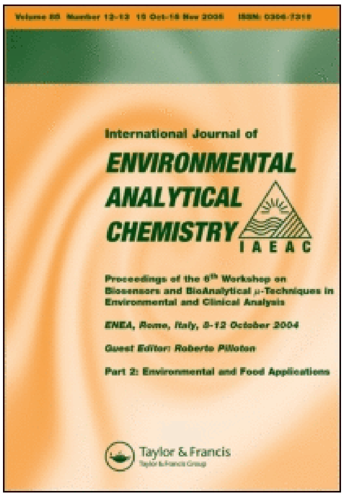

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SIMULTANEOUS DETERMINATION OF CHEMICAL OXYGEN DEMAND/INORGANIC CARBON BY FLOW INJECTION-PERVAPORATION

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A method for the simultaneous determination of chemical oxygen demand (COD) and inorganic carbon by spectrophotometric and potentiometric (pH) detection, respectively, is described. The carbon dioxide is removed by pervaporation and accepted at the upper part of the separation unit by a buffer stream, the pH change of which is measured by a pH-electrode situated on the top of the unit. The donor stream is, at the same time, led to a spectrophotometer for the measurement of COD. The inorganic carbon is calculated as the difference between the total concentration of CO_2 monitored potentiometrically and the COD monitored photometrically. The method was applied to real samples, including paper bleaching liquors, domestic sewage and river water, with good precision. The sampling frequency was 20 h^{-1} for COD determination and 9 h^{-1} for inorganic carbon determination.

Keywords: Chemical oxygen demand; inorganic carbon; pervaporation; flow injection; wastewater

INTRODUCTION

One of the most important characteristics of flow injection is the ease with which on-line separation processes (such as liquid-liquid extraction, dialysis, gas-diffusion, ion-exchange, precipitation and, recently, pervaporation[1–4]) can be implemented, permitting the isolation of the analytes from the matrix and, consequently, avoiding its influence on the measurements.[5]

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Chemical oxygen demand (COD) refers to the oxygen required for the complete chemical oxidation of a water sample. It is an arbitrary empirical measurement obtained by subjecting the sample to oxidation by potassium dichromate or potassium permanganate in acid solution under prescribed conditions. Despite its importance, the manual method has several disadvantages and, therefore, the development of automated methods improving the efficiency of pollution control is necessary. A number of methods has been reported in the literature, referring to the determination of COD by flow injection and using different compounds as COD standards: potassium hydrogenphthalate, D-glucose, sodium oxalate, sodium salicylate and sodium acetate, L-glutamic acid and lactose have been mostly employed. Potassium dichromate in acid solution with conventional heating[6–8] or assisted by microwaves[9] and spectrophotometric detection, or amperometric detection of the I_3^- formed after reaction of the excess of oxidant with potassium iodide;[10] potassium permanganate in acid solution[11–14] and cerium sulphate[15] with heating and spectrophotometric detection in both cases were also used as oxidizing agents.

Carbon dioxide has been determined by gas-diffusion[16–19] and its simultaneous determination with sulphur dioxide has also been reported.[20]

In the present work, the chemical oxygen demand and inorganic carbon are simultaneously determined by making use of the potassium permanganate reaction in acidic medium and spectrophotometric detection for the former and pervaporation integrated with potentiometric detection for the latter.

EXPERIMENTAL

Reagents and Solutions

Sodium oxalate (for analysis, Panreac) was dried at 110–120°C for approximately 1 h; 3.807 g of the dried product were then accurately weighed and dissolved in 250 ml of Milli-Q purified water to prepare a 10 $g \cdot l^{-1}$ stock oxalate solution. All standard solutions were prepared by appropriate dilutions of the stock solution before use. A carbonate stock solution of 10 $g \cdot l^{-1}$ was prepared by dissolving 4.417 g of sodium carbonate (pro analysi, Merck), previously dried at 110°C for 1 h, in 250 ml of purified Milli-Q water. Standard carbonate solutions were prepared by dilutions of the stock one.

A potassium permanganate solution was prepared by dissolving 1.6 g of the solid product (pro analysi, Merck) in 1000 ml of 0.6 M sulphuric acid (purissimum, Panreac); the resulting solution was heated for approximately 1 h at 80–90°C. After cooling at room temperature, it was filtered through a glass filter and standardized by titration with sodium oxalate. Finally, it was stored in an amber-glass bottle, in a dark and cool place. A $1 \cdot 10^{-3}$ M $KMnO_4$ solution was prepared by dilution of the standardized solution with 0.6 M H_2SO_4. An appropriate volume of a 0.01 M manganese (II) solution ($Mn(NO_3)_2 \cdot 4H_2O$, pro analysi, Merck) was added to the $KMnO_4$ solution before dilution to give a final Mn(II) concentration of $2 \cdot 10^{-5}$ M as this cation catalyzes the relatively slow reaction between oxalate and $KMnO_4$.

A 0.6 M H_2SO_4 solution was prepared by dilution of the concentrated reagent in Milli-Q purified water and used as the carrier stream.

A $5 \cdot 10^{-3}$ M $Na_2CO_3/NaHCO_3$ (pro analysi, Merck) buffer solution of pH 9.4 was used as acceptor stream in the pervaporation cell.

A $2 \cdot 10^4$ mg l^{-1} sodium chloride (pro analysi, Merck) solution was prepared and used in the chloride interference study.

PTFE hydrophobic membranes of 1.5 mm thickness, used in the pervaporation unit, were purchased from Trace (Braunschweig, Germany).

Instruments and Apparatus

The hydrodynamic manifold used for the simultaneous determination of COD/inorganic carbon is shown in Figure 1A. It consists of two four-channel Gilson Minipuls-3 peristaltic pumps, fitted with rate selectors (one of the pumps was used for pumping the acceptor stream of the pervaporation cell), a Rheodyne 5041 injection valve and PTFE tubing of 0.7 mm i.d., covered with a transparent varnish to avoid both loss of carbon dioxide to the environment and entrance of it in the system. A waterbath equipped with a T-tronic electronic thermostat (from Atom, Barcelona, Spain) was used to preserve the temperature of the pervaporation unit as required (T-tronic electronic thermostat, atom 131). The pH change of the acceptor stream was monitored by a Crison pH-meter (micro pH 2001), coupled to a flat pH-electrode (Crison), situated on the top of the separation unit. The absorbance values were measured by a Perkin-Elmer Lambda 1 spectrophotometer, furnished with a Hellma 138-QS flow cell (10 mm light path). Both detectors were connected to a double-pen Knauer recorder and the signals obtained in both cases are shown in Figure 1B.

The pervaporation unit[4] was designed in the laboratory and it consisted of a donor and an acceptor chamber and a membrane support. The upper (acceptor) chamber was fitted with a central orifice at its top for the accomodation of the

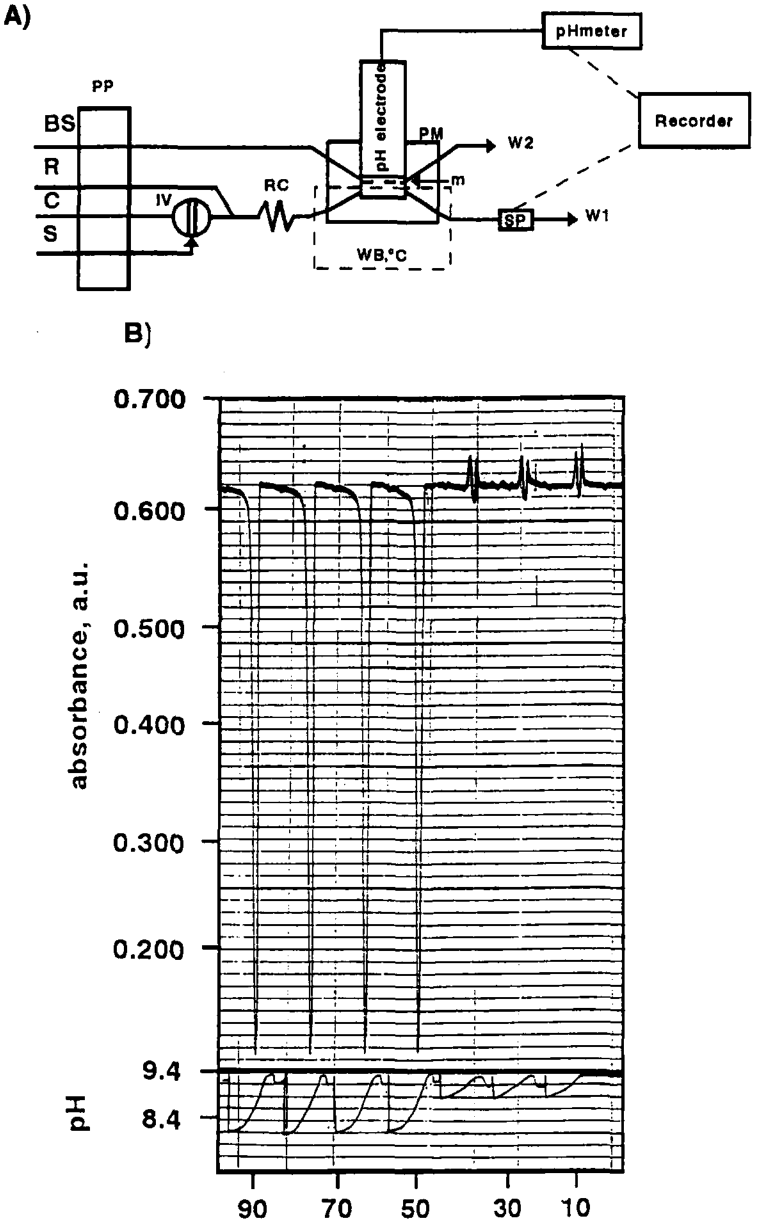

FIGURE 1 (A) Configuration for the simultaneous determination of COD/inorganic carbon. PP: peristaltic pump, BS: CO_3^{2-}/HCO_3^- buffer solution (acceptor stream), R: oxidizing reagent ($KMnO_4$ in H_2SO_4), C: carrier solution (H_2SO_4), S: sample or standard solution, IV: injection valve, RC: reaction coil, PM: pervaporation module, m: membrane, WB: waterbath, SP: spectrophotometer, W: waste. B) Recordings obtained for the simultaneous determination of COD and inorganic carbon.

sensor (pH-electrode) by suitable adaptors. All parts of the module were aligned by inserting metallic rods in the orifices and a closer contact was achieved by screwing them together with four screws between two aluminium supports.

Procedure

The sample or standard solution is injected into a stream of sulphuric acid and it is finally mixed with a potassium permanganate solution (prepared in the same concentration of sulphuric acid, so that the composition of the merged stream in acid is the same as in the individual ones), while passing through a 100 cm coil. The product of the chemical reaction is led to the lower part of the pervaporation module (thermostated at 40°C), from where the carbon dioxide evaporates and diffuses through the hydrophobic membrane and is accepted by a static stream of CO_3^{2-}/HCO_3^- buffer. The change of the pH of this stream is measured by the sensor located at the upper chamber of the separation unit. At the same time, the outlet of the lower chamber is led to the spectrophotometer, where the fading of the colour of the permanganate solution is measured at 525 nm. After the necessary time of stopping of the flow at the upper stream, this is restored so as to remove the carbon dioxide that was accumulated in the stagnant acceptor solution.

RESULTS AND DISCUSSION

All parameters affecting the performance of the system were studied, by the univariate method; their ranges and optimum values are shown in Table I. A standard oxalate solution was used for the optimization study. The analytical

TABLE I Optimization of variables

Parameter	*Range Studied*	*Optimum Value*
H_2SO_4, M	0.15–2	0.6
$KMnO_4$, M	$1 \cdot 10^{-4} - 2 \cdot 10^{-3}$	$1 \cdot 10^{-3}$
pH (acceptor stream)	8.8–10.3	9.4
CO_3^{2-}/HCO_3^- buffer, M	$1 \cdot 10^{-3} - 5 \cdot 10^{-2}$	$5 \cdot 10^{-3}$
Injection volume, μl	200–1500	1000
Reaction coil, cm	50–400	100
Donor flow rate, $ml \cdot min^{-1}$	0.52–1.32	1.10
Temperature, °C	30–46	40

signal used in all instances was the difference between the decrease of the absorbance or pH of the standard solution (or sample) and that of the blank. The study covered the following variables:

Chemical variables: The *concentration of sulphuric acid*, used as both the carrier and the medium in which potassium permanganate was dissolved, was studied in the range between 0.15 to 2 M, by monitoring the decrease of the absorbance as well as that of the pH of the acceptor stream when a standard oxalate solution was injected. Both signals increased with increased sulphuric acid concentrations up to 0.3 M. In the range between 0.3 and 1 M, the signals remained almost constant (r.s.d.% = 1.27, n = 7 for the absorbance signals; r.s.d.% = 1.20, n = 7 for the pH signals) and had the highest value. For H_2SO_4 concentrations higher than 1 M, the signals decreased. A value of 0.6 M was finally chosen for further experiments.

The *concentration of the oxidant* was studied covering the range between $1{\cdot}10^{-4}$ to $2{\cdot}10^{-3}$ M. An increase in the reagent concentration up to $1{\cdot}10^{-3}$ M resulted also in a greater absorbance and pH signals; after this value, a plateau was reached and, finally, a $1{\cdot}10^{-3}$ M solution was used.

$5{\cdot}10^{-3}$ *M* CO_3^{2-}/HCO_3^- *buffer solutions* with varying pH values were used as the acceptor stream in the pervaporation module and the decrease of their pH was monitored by injecting a standard oxalate solution. The decrease was higher for increasing pH values up to 9.15; after this value and up to 9.6, the decrease remained constant, whereas higher pHs gave rise to lower signals.

The *concentration of the buffer solution* affected the analytical signal obtained when highly concentrated buffers were used, as the relatively small concentration of carbon dioxide produced could not provoke a high decrease of the pH of the acceptor stream. On the other hand, extremely diluted buffer solutions gave rise to unstable baseline, due to the dissolution of the atmospheric carbon dioxide in it. In both cases, the decrease of the pH of the acceptor stream was quite low, whereas the best signals were obtained for a buffer concentration of $5{\cdot}10^{-3}$ M.

FI variables: The decrease of both the absorbance of the donor stream and the pH of the acceptor stream was higher, as the *injection volume* increased up to 1000 µl. Higher injection volumes resulted in wider absorbance peaks, causing a lower sampling frequency in the lower stream; however, the heights of both signals remained constant.

The *length of the reaction coil* was also studied over the range 50–400 cm and no influence of it on the absorbance signal was observed, a fact that was attributed to the fast chemical reaction that occurs in the presence of manganese (II) as catalyst. The highest signal for the pH measurements was obtained for a reaction coil length of 100 cm; for higher values a decrease in the height of the signal was obtained, followed by peak broadening.

The only *flow rate* studied was that *of the donor stream*, being the sum of the flow rates of the carrier and reagent streams. No difference in the absorbance signals was observed but low flow rates led to wider signals as dispersion increased. On the other hand, low donor flow rates resulted in a greater pH difference in the acceptor stream, since the residence time of the analyte in the pervaporation unit was longer and, hence, the mass transfer more efficient. Finally, a flow rate of 1.1 $ml \cdot min^{-1}$ (2×0.55 $ml \cdot min^{-1}$) was chosen as the optimum value.

The *flow rate of the acceptor stream* was not studied, since this was stopped during the measurements for the accumulation of the pervaporated carbon dioxide. Measurements were performed at 5, 7 and 10 min; after 7 min, an equilibrium was reached and the signal showed a plateau (Figure 1B). Therefore, this time was used for the following experiments.

Pervaporation variables: The influence of the *temperature* on both analytical signals was studied in the range between 30 and 46°C. The decrease in the absorbance was not affected by the temperature increase, a fact that was attributed to the fast kinetics of the reaction favoured by the presence of the catalyst. An increase of the temperature affects the efficiency of both the evaporation and diffusion processes by increasing the vapour pressure of the analyte and, therefore, increasing the mass transfer through the membrane. As a consequence, a temperature increase up to 40°C gave rise to a higher pH signal; at 46°C, the signal was slightly smaller, probably due to a loss of the electrode sensitivity (the temperature limit for this electrode was 50°C).

Features of the Method

Calibration curves for both the COD and inorganic carbon were run and the values of linear ranges, their equations, correlation coefficients, limits of detection and repeatability are shown in Table II. The first equation corresponds to the decrease of absorbance of the donor stream, and the next two (deriving from a curve described by the equation $y = 4.48 \cdot 10^{-4}x^2 + 0.494x + 0.577$, $r = 0.9974$, after representing the difference of pH as a function of the logarithm of COD concentration) refer to the decrease of pH of the acceptor stream caused by the carbon dioxide produced during the redox reaction. The third one (deriving from a curve described by the equation $y = -2.34 \cdot 10^{-6}x^2 + 3.98 \cdot 10^{-3}x - 0.0165$, $r = 0.99$, after representing the pH difference as a function of the

TABLE II Features of the proposed method

Linear Range, $mg \cdot l^{-1}$	*Equation*	*r*	*l.o.d., $mg \cdot l^{-1}$*	*r.s.d., % (n = 9)*
0.2–18.2[a]	$y = 8.21 \cdot 10^{-3} + 0.029x$	0.9992	0.13	0.56[d]
0.9–9.1[b]	$y = 0.069 + 0.410x$	0.9943	0.45	2.65[e]
9.1–54.6[b]	$y = -0.697 + 1.226x$	0.9992	—	2.41[f]
50–1000[c]	$y = -1.852 + 1.165x$	0.9998	48.6	1.47[g]

[a] spectrophotometric determination of COD; y = absorbance, x = $[O_2]$ in $mg \cdot l^{-1}$
[b] potentiometric determination of carbon dioxide; y = Δ pH, x = log $[O_2]$ in $mg \cdot l^{-1}$
[c] potentiometric determination of carbon dioxide; y = Δ pH, x = log $[CO_3^{2-}]$ in $mg \cdot l^{-1}$
[d] for 14.5 mg $O_2 \cdot l^{-1}$
[e] for 9.1 mg $O_2 \cdot l^{-1}$
[f] for 14.5 mg $O_2 \cdot l^{-1}$
[g] for a CO_3^{2-} solution of 250 $mg \cdot l^{-1}$.

logarithm of CO_3^{2-} concentration) results from the decrease of pH of the acceptor stream caused by the carbon dioxide produced from the reaction of carbonate with the acid. The sampling frequency was 20 h^{-1} for the lower stream and 9 h^{-1} for the upper stream.

Effect of Chloride Concentration

The presence of chloride usually causes positive errors in the COD determination, because it can be oxidized by MnO_4^- to chlorine and, therefore, silver or mercury salts have to be added, so as to avoid the interference.[6,7,11–15] In the present work, the analytical signal of a 20 $mg \cdot l^{-1}$ oxalate solution (or 3.64 mg $COD \cdot l^{-1}$) was recorded and compared to the ones obtained by different solutions, having always the same oxalate concentration and variable concentrations of chloride (of 10, 100, 1000, 5000, 7000 and 10000 $mg \cdot l^{-1}$). No difference in the absorbance was oserved, even when the concentration of chloride was 7000 $mg \cdot l^{-1}$ and without silver or mercury salts. This fact was attributed to both the short reaction time between the interferent and the oxidizing reagent and the relatively mild reaction conditions. For a chloride concentration of 10000 $mg \cdot l^{-1}$, the absorbance increased by 7.4%.

Application of the Method to Real Samples

The carbonate content and the chemical oxygen demand (COD) were determined in white and green bleaching liquors, after appropriate dilution. As very low concentrations of oxidizable organic compounds are present in these samples, the signal corresponding to the released carbon dioxide was entirely attributed to carbonate and calculated as such. The chemical oxygen demand calculated for these samples refers mostly to inorganic reductants, mainly sulphide and sulphite. The target analytes were determined in water samples of different origin by direct aspiration. The results obtained are shown in Table III. It was unfeasible to do the recovery experiments for the last samples because the addition of the oxalate caused precipitation of calcium oxalate (the samples were quite alkaline). The results in the case of carbon dioxide determination are expressed as carbonate concentration.

CONCLUSIONS

The method proposed here can be easily implemented in on-line simultaneous monitoring of COD and inorganic carbon in wastewater and its more important features are as follows:

Automation of the overall procedure can be accomplished with very low both acquisition and maintenance costs.

The sensitivity, selectivity and precision are sufficient for the systems to which it must be applied as is the sample throughput. In addition, continuous monitoring can be implemented if required by removing the injection valve and aspirating the sample instead the carrier solution.

TABLE III a) Application of the method to real samples a) COD determination (mg $O_2 \cdot l^{-1}$)

Sample	*Found, mg·l⁻¹*	*Recovery, % (r.s.d., %, n = 3)*	
		Addition of 9.1 mg·l⁻¹	*Addition of 14.5 mg·l⁻¹*
Green bleaching liquor 1[a]	2.46	102.2 (1.73)	99.1 (0.18)
Green bleaching liquor 2[b]	1.75	107.9 (0.29)	101.5 (0.18)
White bleaching liquor 1[a]	2.40	101.6 (1.01)	93.9 (0.39)
White bleaching liquor 2[b]	1.65	102.1 (0.79)	95.1 (0.19)
Sewage collector (Alcolea)	2.36	92.06 (1.07)	94.6 (0.23)
Guadalquivir river (Puente Romano, Córdoba)*	0.26	—	
Mixture: sewage collector-river stream (Alcolea)*	0.27	—	—

[a] dilution 1:3500
[b] dilution 1:4500
*recovery experiments were not feasible, as explained in the text

TABLE III b) Inorganic carbon determination (mg $CO_3^{2-} \cdot l^{-1}$)

Sample	*Found, $mg \cdot l^{-1}$*	*Recovery, % (r.s.d. %, n = 3)*	
		Addition of 50 $mg \cdot l^{-1}$	*Addition of 80 $mg \cdot l^{-1}$*
Green bleaching liquor 1[a]	196.6	94.4 (0.82)	94.2 (0.54)
Green bleaching liquor 2[b]	84.0	104.5 (1.46)	94.9 (1.04)
White bleaching liquor 1[a]	50.0	100.0 (1.25)	93.3 (0.73)
White bleaching liquor 2[b]	(nd)	101.8 (1.04)	91.8 (0.75)
Sewage collector (Alcolea)	187.5	102.7 (1.13)	95.5 (1.56)
Guadalquivir river (Puente Romano, Córdoba)*	271.4	—	—
Mixture: sewage collector-river stream (Alcolea)*	163.6	—	—
River stream Guadalbarbo (Alcolea)*	154.4	—	—

[a] dilution 1:300
[b] dilution 1:500
*recovery experiments were not feasible, as explained in the text
(nd) not detected

The main advantage of the use of pervaporation as alternative to gas-diffusion for the removal of CO_2 is that the donor solution never comes into contact with the membrane thus overcoming drawbacks such as its clogging and fast deterioration, which can be crucial in automated systems.

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