Determination of chemical oxygen demand by a flow injection method based on microwave digestion and chromium speciation coupled to inductively coupled plasma optical emission spectrometry

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ABSTRACT

The present paper evaluates the applicability of a new FIA system for COD determination. The new system, flow injection microwave solid phase extraction by means of activated carbon (FI-MW-SPE), consists of a digestion circuit, placed in a home MW oven, coupled to an ICP-OES spectrophotometer. Doehlert experimental design was used to speed up the optimization of different experimental variables studied for assisted digestion methods. The method provided a high throughput of about 18 samples h^{-1}. To assess the accuracy of analytical methods linear regression, elliptic joint confidence region (EJCR) was used. A large linear range of 2.78–850 mg O$_2$ L^{-1} with an excellent detection limit of 0.94 mg O$_2$ L^{-1} was obtained. The interference by high chloride concentration was studied, and values below 3000 mg Cl$^-$ ions L^{-1}, allowed the estimation of COD load without any masking agents. COD values for various types of wastewater samples were correlated with those obtained by standard manual methods. Moreover, interferences due to matrix nature are absent; since matrix is washed out of the column before Cr (III) is eluted. This method reduces the time, reagent volume, hazardous emission, external contamination, with a good reproducibility and accuracy.

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1. Introduction

The most relevant pollution impact of domestic wastewaters results from organic matter. The organic matter content in wastewater can be determined by using a variety of analytical methods. At levels above 1 mg L^{-1}, this quantity can be estimated by determining parameters such as total organic carbon (TOC), biological oxygen demand (BOD) or chemical oxygen demand (COD) [1]. TOC is a generic measurement which relies on specific instruments; BOD is related to carbon-source biodegradation needs and COD represents the chemical oxidability [2]. However, COD is the most widely used in the characterization of polluting aqueous effluents [3]. COD provides a good balance between the value of the information gained and the speed of analysis when compared to the BOD and TOC tests. COD gives the amount of oxygen necessary to oxidize all the organic matter of this sample. Usually, for COD determination, the organic matter contained in a given sample of water is oxidized by adding a known excess of a strong oxidant. A commonly used oxidant in COD assays is potassium dichromate (K$_2$Cr$_2$O$_7$) which is used in combination with boiling H$_2$SO$_4$. After a refluxing digestion step, carried out normally in open containers, the remaining excess of oxidant is titrated or the amount of Cr (III) generated by reduction of Cr (VI) is determined spectrophotometrically [4]. These methodologies suffer from a series of drawbacks: (a) analysis time is too long, 2 h being required for digestion plus time for the titration; (b) the number of stages in the procedure increase the probability of errors; (c) there is a quite high consumption of expensive (Ag$_2$SO$_4$) and toxic (HgSO$_4$) chemicals; and (d) different inorganic species (Cl$^-$, NO$_2^-$, Fe (II), etc) cause interferences on this method.

Several modifications have been proposed to circumvent these drawbacks. In order to reduce the chloride-ion interference, the mercury salt (e.g. HgSO$_4$) is usually added to mask the chloride ion. Jirka and Carter [5] introduced a micro semi-automated method in which digestion is carried out in sealed glass tubes. They used the same sample to reagents ratio and the same digestion time as was used in the reference method, but Cr (III), instead of Cr (VI), was colorimetrically determined. However, turbidity of the reaction mixture, caused by inorganic particulate substances present in some surface water samples, increased the absorbance, causing a positive error in the determination [6].

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In spite of the advantages of the semi-micro method, the digestion time is too long. This drawback has led to the development of some COD determination methods in which digestion is carried out by flow injection analysis (FIA). In this context, Microwave Assisted Digestion (MAD) becomes a fair option to be applied in COD determination methods.

Smaller differences between microwave and reflux methods were obtained in a combined program by House and Krišťnrová [7]. Interference by chlorides, however, was considerable despite their binding with Hg^{2+} ions. Results with real waters were lower than with the reflux method. In COD microwave determinations, Cr^{3+} ions do not seem to produce a resistant complex with chlorides in a strongly acid oxidizing medium, but merely reduce the reaction rate of chloride oxidation—the same as with oxidation of some substances under observation. The use, therefore, of a lower energy value of microwave source together with longer exposure seems to be more advantageous [8].

Microwave heating systems afford efficient transfer of energy and substantially reduce heating time; also, it allows the process to be more accurately controlled and completely automated in a straightforward manner [9,10]. In addition the introduction of MAD into FI systems enhance these advantages.

FIA systems improves measurements through fast sampling and cleaning of the measurement devices; fast analytical control of the baseline/background; an easy and rapid standardization; improved repeatability; a considerable reduction of reagent, solvent consumption and waste generation; and a possible enhancement of the analytical sensitivity through the online coupling of detection with preconcentration/separation techniques.

FIA combined with inductively coupled plasma (ICP) [11,12]; flame atomic absorption spectrometry (FAAS) [13,14] and electrothermal atomic absorption spectrometry (ETAAS) [15,16] are the most used techniques in the determination of chromium. However, to our knowledge, ICP-OES has not yet been applied to the determination of COD. In addition, Cr (III) and Cr (VI) must be separated before reaching the spectrophotometer (speciation). The separation of both Cr species has been undertaken in several ways. For example, Cavaco et al. [17] used different types of resins (Amberlite IRC 748, Diaion CR 11 and Diphonix) in order to retain Cr (III). After its elution, Cr was determinate by FAAS. Liang and Sang [18] developed a novel method for the determination of Cr (III). It was based on cloud point extraction (CPE) separation and preconcentration, and determination of Cr (III) was determined by graphite furnace atomic absorption spectrometry (GFAAS).

The aim of this work was to develop and optimize a method to asses COD in water samples, avoiding high reagent and time consuming operations. This was achieved joining MAD and SPE system into a FI methodology. Chromium was retained in the form of Cr (III) by sorption on a minicolumn packed with activated carbon (AC) in the absence of a complexing reagent, as previously described [19]. The determination was performed by ICP-OES associated with a flow injection (FI) methodology. For increased flexibility and robustness, power control (temperature) and sample flowing rates (reaction time) were optimized by a multivariate response surface method. The results obtained for reference substances, river water and urban wastewater were compared with those provided by a closed reflux method described in the Standard Method (5220 D) [4].

2. Experimental

2.1. Reagents

Reagents were prepared as described in the Standard Method [4] for the closed reflux method. All reagents were of analytical grade. Double-distilled and ultrapure (18.2 Mohm cm) water was used throughout.

The activated carbon (Merck, Darmstadt, Germany, 50–70 mesh) was used after pretreatment with acid. Activated carbon was heated with 10% (v/v) hydrochloric acid for 30 min and then with 10% (v/v) nitric acid for 20 min and finally washed with deionized water until neutral pH was reached [19].

Buffer solutions were prepared by diluting a 2.0 mol L^{-1} acetic acid solution adjusted to pH 5.0 with sodium hydroxide [19].

Blank determinations were carried out on double-distilled water.

2.2. Samples

Synthetic samples of potassium acid phthalate (KHP) with a theoretical COD of 1000 mg $O_2 L^{-1}$ and glucose (500 mg $O_2 L^{-1}$) were used as standards. KHP is used as the internationally accepted standard for this determination. Appropriate dilutions gave solutions of different COD values [4]. River water was used as natural sample; with a COD of 25 mg $O_2 L^{-1}$. A wastewater (effluent from domestic sewage) with a COD above 2000 mg $O_2 L^{-1}$ was used. However, prior to digestion, sample was diluted to a final COD value under 1000 mg $O_2 L^{-1}$, filtered through a 0.45 μm membrane and preserved with sulfuric acid.

2.3. Column preparation

The conical minicolumn was prepared by replacing 30 mg (30 mm length, 5 mm internal upper-diameter and 2 mm internal lower-diameter) of AC into an empty conical tip using the dry packing method. To avoid loss of AC when the sample solution passed through the conical minicolumn, a small amount of quartz wool was placed at both sides of the conical minicolumn. The column was then connected to a peristaltic pump with PTFE tubing to complete the preconcentration system.
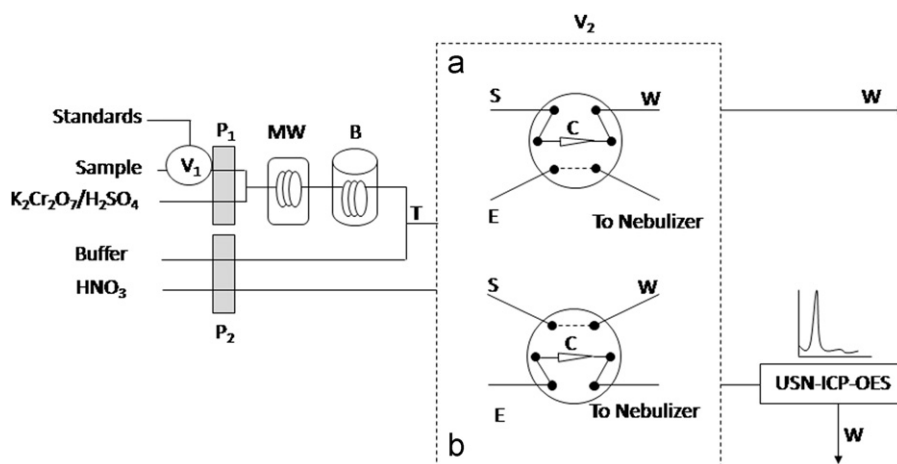
2.4. Instrumental

Tubing of PTFE was used throughout, except in the peristaltic pump. Tygon type tubings were not employed since they did not have enough chemical resistance during the microwave induced oxidation (Section 2.5). Pump tubes-Tygon type (Ismatec, Cole-Parmer Instrument, Niles, IL, USA) were only employed to propel the sample and eluent. The flow injection system consisted of 2-way peristaltic pump (Gilson Minipulse, Villiers-Le-Bell, France), a 4-way injection valve (Rheodine Model 50, Cotati, CA, USA). A domestic MW oven (Philco, mod. KOR 636T) was used without modification.

The measurements were performed with an ICP-OES [BAIRD (Bedford, MA, USA) ICP 2070]. The 1 m-Czerny Turner monochromator had a holographic grating with 1800 grooves mm^{-1}. The 357.9 chromium wavelength was used and measurements of the FI system were expressed as peak height, which was corrected against the reagents blank. The ICP operating conditions are listed in Table 1.

Table 1
ICP-OES instrumental parameters employed for chromium determination.

Forward power	1.0 kW
RF generator	40.68 MHz
Nebulizer	Glass, Meinhard
Coolant gas flow rate	8.5 L min^{-1}
Auxiliary gas flow rate	1.0 L min^{-1}
Carrier gas flow rate	0.5 L min^{-1}
Solution uptake rate	1.5 mL min^{-1}
Observation height (above load coil)	15 mm

Fig. 1. Schematic diagram of the instrumental set up: S, sample; B, buffer; E, eluent; W, waste; P_1 and P_2, peristaltic pump; MW, microwave oven; B, 4 °C-ice bath; T, sample and buffer line connector; C, minicolumn packed with activated carbon; V_1 and V_2, injection valves. Valve 1 positions: (a) loading; (b) injection.

2.5. Procedure and determination

A scheme of the manifold employed is shown in Fig. 1. Before start the reaction/preconcentration cycle, the conical mini-column and the tubing were washed with ultrapure water.

2.5.1. Reaction and loading

2 mL aliquot was sampled in a time-based mode. Sample solutions and the oxidizing solution flowed through different lines and merged just before the microwave oven where the reaction occurred (Valve V_1 in position A). The resulting solution was cooled in an ice bath (4 °C) and this flow was injected through a "T" connector, within a 10-times higher flow of a buffer solution (pH 5.0). This stream flowed throughout the AC mini-column with valve V_1 in position S and valve V_2 in load position (a) to allow the retention of Cr (III) (elapsed time 2.83 min).

2.5.2. Injection/Data acquisition

After loading, the sample line (S) was emptied, whilst the buffer solution line remained in flow. The peristaltic pump (P_1) was stopped and the injection valve V_2 was switched to the injection position (b). In this step, the HNO_3 solution that passed through the conical minicolumn, eluting Cr (III), and introducing it to the detector. At this point, the signal monitored in the ICP spectrometer could be recorded as peak height, which was proportional to the amount of Cr (III) retained, which in turn, was proportional to the organic matter in the sample (elapsed time 0.84 min).

The operating conditions were established and the determination carried out, either with reagent blanks, calibration standards, spiked samples, and real samples.

In this way, determination of COD by a flow injection method based on microwave digestion and chromium speciation (solid phase extraction) (FI-MW-SPE) is obtained.

The emission measurements were proportional to the chromium (III) concentration in the sample and COD.

3. Results and discussion

3.1. Optimization of digestion time and liquid flow

Chlorides are the chief source of trouble when determining COD [20]; for this reason, special care must be taken in the measurement of organic matter in samples with chlorides higher than 2000 mg L^{-1}. This is due to the oxidation of chloride ions expressed by the following equation:

$$Cr_2O_7^{2-} + 6Cl^- + 14H^+ \rightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O \tag{1}$$
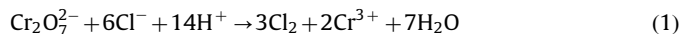
The standard method [4] suggests using a $HgSO_4$:Cl ratio equal to 10:1 when chloride concentration is up to 2000 mg L^{-1} in order to mask the excess of chloride by the formation of $HgCl_2$.

According to Dasgupta and Petersen [21], the reaction of $K_2Cr_2O_7$ with KHP follows a second-order rate low:

$$-d\left[Cr_2O_7^{2-}\right]/dt = kn\left[Cr_2O_7^{2-}\right][Org] \tag{2}$$

$$-d[Cr_2O_7^{2-}]/dt = kn[Cr_2O_7^{2-}][Cl^-] \tag{3}$$

This shows that the rate of the reaction of $K_2Cr_2O_7$ with Cl (3) is taking place at a lower rate than the reaction with organics (2).

In COD microwave determinations, Cr^{3+} ions do not form a resistant complex with chlorides in a strongly acid oxidizing medium, but merely reduce the reaction rate of chloride oxidation. The use, therefore, of a lower energy value of microwave source together with longer exposure seems to be more advantageous (Houser and Majíčková) [22]. Thus, it becomes necessary to optimize the working conditions.

The use of Doehlert experimental design locates critical point (maximum, minimum and saddle points) at each step of the procedure finding the experimental region in which the next design, if necessary, should be constructed [23,24]. In this work this response surface method has been applied to the optimization of the main variables involved (flow rate and MW power). This design is suitable for the location of an optimum set of experimental conditions from a very good fitting of a quadratic model. The seven experiments required for the Doehlert matrix are shown in Table 2. The emission signal (peak heights) obtained in this experiment was expressed as COD and used then to feed the Doehlert matrix and the obtained surface response is shown in Fig. 2. All data were processed using Design-Expert 8.0.6 (Trial version).

The results obtained (as real values, not codified) fit to the following equation:

$$COD = -1511.23723 + 401.56758*Flow\ rate + 1.83624*MW\ power$$
$$-29.41716*Flow\ rate^2 - 2.463 \times 10^{-3}*MW\ power^2 \tag{4}$$

which illustrates the relationship between the COD the flow rate and MW power. To obtain maximum values for a theoretical COD of 200 mg O_2 L^{-1} the optimal value are flow rate 6.64 mL min^{-1} and MW power 360 W. As can be seen, these values fall within the experimental area; however our microwave system does not allow us to operate under these conditions, so the linear

Table 2
Factor levels, design matrix and response from 2^2 factorial design for COD microwave assisted digestion method optimization. KHP was added with a theoretical COD value of 200 mg L^{-1}.

Factors			Levels	
			(−) Low	(+) High
Flow rate (FR, mL min^{-1})			5	9
MW power (MWP, W)			150	550
Run	**FR**	**MWP**	**COD**[a]	**Variance**
1	−1	0	111.46	2.77
2	−0.5	−1	55.43	2.02
3	−0.5	+1	89.05	1.28
4	0	0	199.25	4.48
5	+0.5	−1	42.36	3.20
6	+0.5	+1	98.39	2.40
7	+1	0	51.7	3.36

[a] Number of replicates=5.
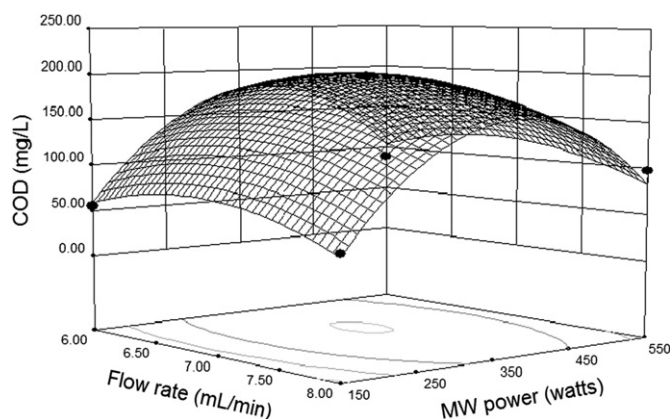
Fig. 2. Estimated COD function (surface response) for flow rate and MW power (Experimental results are represented by the black balls on the graph).

Table 3
COD determination by the standard method and FI-MW-SPE method.

Theoretical COD using KHP (mg L^{-1}) (A)[b]	Determination of COD (mg L^{-1}) by		Ratio		CV[a] (%)	
	Standard method (B)[b]	Proposed method (C)[b]	B/A	C/A	Standard method (B)	Proposed method (C)
0	2.1 ± 0.29	1.1 ± 0.27			13.96	24.6
10	10.7 ± 0.11	10.1 ± 0.13	1.05	1.01	1.04	1.24
20	22 ± 0.46	20.6 ± 0.45	1.09	1.03	2.11	2.18
50	51.7 ± 0.24	20.4 ± 0.48	1.03	1.01	0.46	0.95
100	102.3 ± 1.48	100.3 ± 0.69	1.02	1.00	1.44	0.69
200	203.2 ± 1.27	201.3 ± 1.26	1.01	1.01	0.62	0.62
500	503 ± 1.49	502 ± 1.38	1.01	1.02	0.29	0.27
850	854 ± 1.24	852.5 ± 1.83	1.01	1.01	0.14	0.21

[a] Coefficient of variance.
[b] Mean ± SD, n=3.

Fig. 3. Confidence intervals based on WLS method (α=0.05) (—: EJCR, ∗: Ideal Point).

calibration curves were constructed using a flow rate equal to 7 mL min^{-1} and MW power equal to 350 W, which ensured optimal responses as well.

3.2. Regression analysis of FI-MW-SPE

The proposed method, FI-MW-SPE, was applied to the quantification of COD range between 10 mg O$_2$ L^{-1} and 850 mg O$_2$ L^{-1}. For calibration purposes, seven concentration levels (10, 20, 50, 100, 200, 500 and 850 mg O$_2$ L^{-1}) were prepared and calibration curve was built using standard solutions of KHP. Each level of concentration was made in quintuplicate. Standard method and FI-MW-SPE method were compared (Table 3); the standard deviation and coefficient of variance of the results reveals that the proposed method is efficient with greater repeatability. Under the optimum conditions described above, the calibration graph of peak heights (P) vs. COD was linear in the range of 2.8–850 mg O$_2$ L^{-1} with the regression equation of P=1199.3 COD (mg O$_2$ L^{-1})+721.9 (r=0.997). The relative standard deviation (RSD) was 0.30%, calculated from the peak heights obtained. The limit of detection (LoD) and the limit of quantification (LoQ), calculated as the concentration of organic matter required to yield a Cr (III) concentration equal to three and ten times the standard deviation of the blank records, were 0.94 mg O$_2$ L^{-1} and 2.78 mg O$_2$ L^{-1} when 1 mL of sample solution was processed. Lower LoD and LoQ could be achieved if higher sample volume is processed.

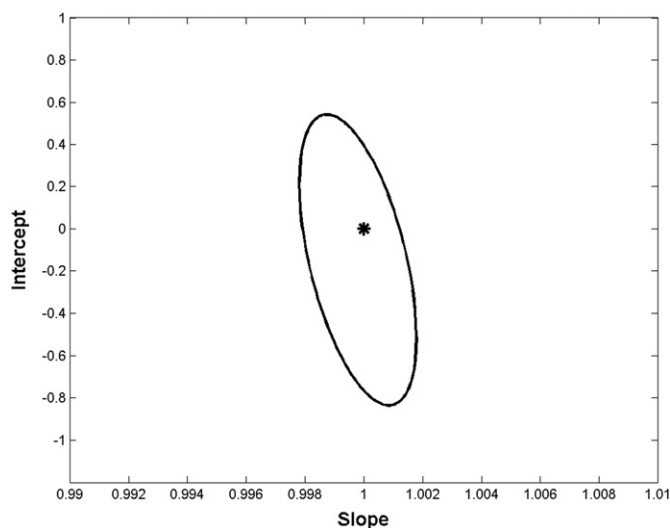To assess the accuracy of analytical methods using linear regression, elliptic joint confidence region (EJCR) for the true (β) slope and intercept (α) was used. The center of ellipse is (a, b). Any point (a, b) which lies inside the EJCR is compatible with the data at the chosen confidence level P. In order to check the new method, the values α=0 and β=1 were compared with the estimates (a) and (b) using the EJCR. If the point (0, 1) lies inside the EJCR, then bias are absent. Under these conditions the application of the process shows if the joint confidence interval test based on the regression technique provides correct results [25,26].

In order to test if the slope and intercept are not different from the idealistic values α=0 and β=1 simultaneously, the procedure based on the EJCR was considered. Fig. 3 shows these regions calculated for WLS technique. The plot of $x_{\text{COD standard}}$ versus $x_{\text{FI-MW-SPE assisted}}$ was linear with an intercept of −0.145 and a slope of 0.9998 (±0.0012). The correlation coefficient was about 0.9999 and the regression variance s^2=0.0043 and RMSE (root mean square error)=0.3058. The point (0, 1) lies inside the EJCR (p-value < 0.05), which leads to consider that new method is comparable to standard method.

3.3. Interference by chlorides

The interference due to chloride ion was studied by adding chloride ions (1000 and 3000 mg Cl$^-$ ions L^{-1}) in the standard solution of KHP without HgSO$_4$. The samples were subjected to

COD determination by the standard method and proposed method under the optimal conditions selected (flow rate-$=7\text{ mL min}^{-1}$ and MW power$=350$ W). The results are shown in Table 4 and indicate that the chloride ion did not interfere below 3000 mg Cl$^-$ ions L^{-1} in the estimation of COD load; however by the standard procedure, it is reported that chloride ions are interfering above 2000 mg Cl$^-$ ions L^{-1}. Thus, the potential of the *FI-MW-SPE* method is higher for the oxidation process.

3.4. Recovery study and application to real samples

Both microwave digestion and closed reflux digestion [4] were used to determine the COD values of glucose and water samples, which included river water and wastewater samples to evaluate the applicability of the focused microwave digestion method. All samples were analyzed repeatedly with filtration by both the conventional closed reflux method and the newly developed FI-MW-SPE method. Using this method, 4 samples (three replicates) can be determined. Digestion and determinations take 60 min approximately for all.

The data listed in Table 5 shows that the obtained results by both methods are comparable. Spike-recovery tests were performed for different samples as follows: a solution of KHP was added. The accuracy of the proposed methodology was then evaluated as recoveries of the spikes as 100[(found value−base value)/added amount]. The results were always better than 96%, showing that the procedure is accurate.

3.5. Application to other organic compounds

The COD values of various pure organic compounds were determined by the standard method and FI-MW-SPE method. The results are given in Table 6. For comparison purposes theoretical values are also included in Table 6. The recovery values are in the range of 97.7%–99.4%, 68%–101% and 96.4%–98.8% for classical and FI-MW-SPE method, respectively.

4. Conclusions

A novel determination of COD by a flow injection method based on microwave digestion and chromium speciation by solid phase extraction (FI-MW-SPE) has been proposed and experimentally validated. The developed method provided a high throughput of about 18 samples h^{-1}, meeting with the requirement of large-scale environmental assessment.

Doehlert experimental design speeds up the experimental variables' optimization of the FI-MW-SPE method.

Moreover, the method covers a large linear range (2.78–850 mg O$_2$ L^{-1}) with an excellent detection limit of 0.936 mg O$_2$ L^{-1}. The method can also be used to determine high COD sewage water by approximately dilution of the water samples.

FI-MW-SE allows samples with high chloride concentration to be handled without the need of adding HgSO$_4$. Moreover, interferences due to matrix nature are absent; since matrix is washed out of the column before Cr (III) is eluted.

FI-MW-SE is a simple, automatic and environmentally friendly method successfully applied to the determination of COD in real water samples becoming a promising tool for water quality controls.

Table 4
Effect of the chloride ion concentration on COD determination in KHP samples by FI-MW-SE method.

COD (mg L^{-1})[a]			
Theoretical	Distilled water[b]	+1000 mg L^{-1} Cl$^-$[b]	+3000 mg L^{-1} Cl$^-$[b]
10	10.2 (1.6)	10.3 (1.8)	10.8 (3.9)
50	50.6 (2.3)	50.8 (2.5)	51.7 (2.9)
100	100.6 (2.2)	101.4 (3.1)	103.2 (3.8)
200	201.6 (3.1)	201.3 (2.7)	204.5 (3.2)

[a] Number of replicates=5.
[b] Mean ± SD.

Table 5
Recoveries in COD values with spike test in different samples.

Sample	Standard method[a]				FI-MW-SPE method[a]			
	COD (mg L^{-1})			Recovery (%)	COD (mg L^{-1})			Recovery (%)
	Initial	Added[b]	Found		Initial	Added	Found	
Domestic sewage[c]	283 ± 6	100	382 ± 3	99	285 ± 6	100	382 ± 2	98
Dairy wastewater[c]	476 ± 8	150	620 ± 3	96	478 ± 8	150	623 ± 2	97
Dyes wastewater[c]	726 ± 7	150	870 ± 3	96	728 ± 7	150	872 ± 3	96
River water (low salinity)	27 ± 2	25	52 ± 2	98	29 ± 1	25	54 ± 1	99
River water (high salinity)	35 ± 2	25	59 ± 2	96	37 ± 2	25	61 ± 2	97

[a] Mean ± SD, n=5.
[b] Organic matter as KHP.
[c] Samples analyzed after stepwise dilutions.

Table 6
Comparison between the COD values and their relative standard deviations for several compounds by the FI-MW-SPE method and the reference method[a].

Compound	Theoretical value	Standard method			FI-MW-SPE method		
	COD (mg L^{-1})	COD (mg L^{-1})	RSD (%)	Recovery[b] (%)	COD (mg L^{-1})	RSD %	Recovery[b] (%)
Acetic acid	102.8	102.2	0.21	99.4	101.5	0.41	98.7
Lactic acid	100.8	99.2	0.45	98.4	98.4	0.67	97.6
Oxalic acid	99.7	98.3	0.59	98.6	98.7	0.46	98.8
Picric acid	100.2	99.6	0.22	99.4	98.8	0.85	98.6
Salicylic acid	101.8	99.4	0.34	97.7	98.2	0.49	96.4

[a] Number of replicates=5.
[b] 100∗(found/theoretical value).

Acknowledgments

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