Automatic flow analysis method to determine traces of Mn2þ in sea and drinking waters by a kinetic catalytic process using LWCC-spectrophotometric detection

Laura Chaparro, Laura Ferrer, **Luz O. Leal**, Víctor Cerdà

Abstract

A new automatic kinetic catalytic method has been developed for the measurement of Mn^{2+} in drinking and seawater samples. The method is based on the catalytic effect of Mn^{2+} on the oxidation of tiron by hydrogen peroxide in presence of Pb^{2+} as an activator. The optimum conditions were obtained at pH 10 with 0.019 mol L^{-1} 2'2 bipyridyl, 0.005 mol L^{-1} tiron and 0.38 mol L^{-1} hydrogen peroxide. Flow system is based on multisyringe flow injection analysis (MSFIA) coupled with a lab-on-valve (LOV) device exploiting on line spectrophotometric detection by a Liquid Waveguide Capillary Cell (LWCC), 1 m optical length and performed at 445 nm. Under the optimized conditions by a multivariate approach, the method allowed the measurement of Mn^{2+} in a range of 0.03–35 µg L^{-1} with a detection limit of 0.010 µg L^{-1}, attaining a repeatability of 1.4% RSD. The method was satisfactorily applied to the determination of Mn^{2+} in environmental water samples. The reliability of method was also verified by determining the manganese content of the certified standard reference seawater sample, CASS-4.

1. Introduction

The concentration of manganese in the ocean crust is about 60% higher than that in the continental one [1]. Mn^{2+} is a biometal with low contents in natural waters. Manganese enters living organisms from the environment, in which it is present

mainly as hydrated Mn^{2+}. The latter can be oxidized under aerobic conditions to give $Mn(III)$ or $Mn(IV)$, which form soluble and insoluble compounds. The concentration of manganese in natural waters varies from 0.1 to 130 µg L^{-1}, in sea waters 0.03–0.8 µg L^{-1} and tap water up to 1 mg L^{-1}[2]. Thus, Mn^{2+} present in natural waters always participate in biocycles, and it is the most studied trace element in the marine environment [3] ; [4].

The kinetic catalytic method is one of the most attractive methods for the analysis of trace metals since it offers high sensitivity and simplicity. Thus, ultra-trace levels of metal ions, which act as a catalyst in the reaction, may be appropriately determined with a simple instrumentation [5] ; [6]. Many kinetic methods have been reported for the determination of manganese based on their catalytic effects on the oxidation of compounds by various oxidizing dyes [7]; [8]; [9] ; [10]. Some methods for the determination of Mn^{2+} based on kinetic catalytic process have been reported in order to analyze waters samples [11]; [12] ; [13]. Although some of these methods are sensitive, must be performed at a higher temperature or take a longer time for each analysis.

The automation degree of these methods, i.e. the instrumental development for both detection and data acquisition, has been and it is crucial in the search for greater efficiency and extends the application of catalytic kinetic methods. The emergence of flow analysis techniques has provided significant benefits, not only the drastic reduction of the volumes of reagents and samples used, but also for automation capabilities and to maintain stable and reproducible reaction conditions during the analytical process. Multicommuted flow systems have some advantages

such as high accuracy, elevated sample frequency, high degree of flexibility, manipulation of micro-volumes, minimization of reagent consumption and waste generation [14].

The multisyringe flow injection (MSFIA) consists in an automatic burette with a piston that moves simultaneously four syringes embolus, and on the head of each syringe there is a three-way solenoid valve of fast switching. MSFIA allows to increase the versatility of the proposed technique and to reduce reagents consumption [15]. Furthermore, additional devices can be connected to the flow-based system using a network of tubes, usually polytetrafluoroethylene (PTFE) tubing, which allows the flow of the liquids, their mixture and be directed to detection systems [16].

The lab-on-valve (LOV) is a monolithic piece with a central channel connected with peripheral ports, mounted atop a selection valve [17]. LOV is connected with MSFIA module via a holding coil for liquid manipulating operations [18]. In addition to compactness, LOV system ensures repeatability of microfluidic manipulations thanks to the permanent rigid position of the sample processing channels [19].

The limitations associated with low sensitivity in spectrophotometric detection can be solved by using a liquid waveguide capillary cell (LWCC). The emerging potential of LWCC for the determination of chemical special at low concentrations enhances the capability to investigate environmental processes and monitor environmental systems [20].

Thus, in this work a LWCC was coupled to a MSFIA-LOV system to develop an automatic, rapid and sensitive method to determine Mn^{2+} in waters, exploiting a

spectrophotometric detection at 445 nm. This paper describes the methodology to determine traces of manganese, based on the catalytic effect of Mn^{2+} on the oxidation of tiron by hydrogen peroxide in presence of Pb^{2+} as an activator, using a cationic resin for on line sample clean-up.

2. Experimental

2.1. Reagents and solutions

All chemicals used were of analytical reagent grade. All aqueous solutions were prepared using Millipore water. Working standard solutions of Mn^{2+} and Pb^{2+} were prepared daily by dilution of a 1000 µg L^{-1} stock solution (ultra-pure, Scharlau, Barcelona, Spain) in 0.01 mol L^{-1} of nitric acid.

Buffered reagent was prepared with borax ($Na_2B_2O_7 \cdot 10H_2O$) (99.5% for analysis, Acros organics). The pH adjustment was done by addition of ammonia (28%, reagent grade, Scharlau). A solution of 0.0195 mol L^{-1} of 2,2-bipyridyl (99%, Fluka Chemika), 0.38 mol L^{-1} hydrogen peroxide (30% extra pure, Scharlau) and 0.005 mol L^{-1} of 4,5-dihydroxy-1-3-benzenedisulfonic acid disodium salt monohydrate (97% Tiron, Fluka Analytical) were prepared daily. Resin Dowex® 50 WX8 (100-200 mesh; SERVA Electrophoresis GmbH) was used to carry out the on line sample clean-up.

The study of interferences was carried out with cations and anions present in drinking and seawaters. Thus, working standard solutions prepared from standard stock solutions of 1000 mg L^{-1} of Cd^{2+} (metal), Ca^{2+} ($CaCO_3$), Mo^{2+} ($Mo(NO_3)_2$), Mg^{2+} (metal), Fe^{2+}(Na_2Fe), Zn^{2+} (metal), Ni^{2+} ($Ni(NO_3)_2$), Cu^{2+} (metal), Al^{3+} (metal), Co^{2+} ($Co(NO_3)_2$), Cr^{3+}($Cr(NO_3)_3$), K^+ (KCl) (ultra pure standards, Scharlau, Barcelona,

Spain) were used for evaluating cation interferences, while salts of magnesium sulphate ($MgSO_4 \cdot 7H_2O$, Scharlau) and magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, Merck) were prepared for checking nitrate and sulfate interferences.

The materials and vessels used for samples or standards were stored in 10% (v/v) nitric acid for at least 24 h, and rinsed with Millipore water prior to use.

2.2. Samples

The proposed method was applied to different types of water samples, seawaters from different location (harbors, open sea and coastal area), mineral water and tap water. Only the seawaters were previously filtered through 0.45 µm pore size. Samples were acidified with 0.01 mol L^{-1} HNO_3 and injected directly into the system. The seawater certified reference material CASS-4 from the National Research Council of Canada was directly analyzed.

2.3. Manifold and software

A scheme of the MSFIA-LOV-LWCC-UV–vis system is shown in Fig. 1. The system is constituted by a multisyringe burette with
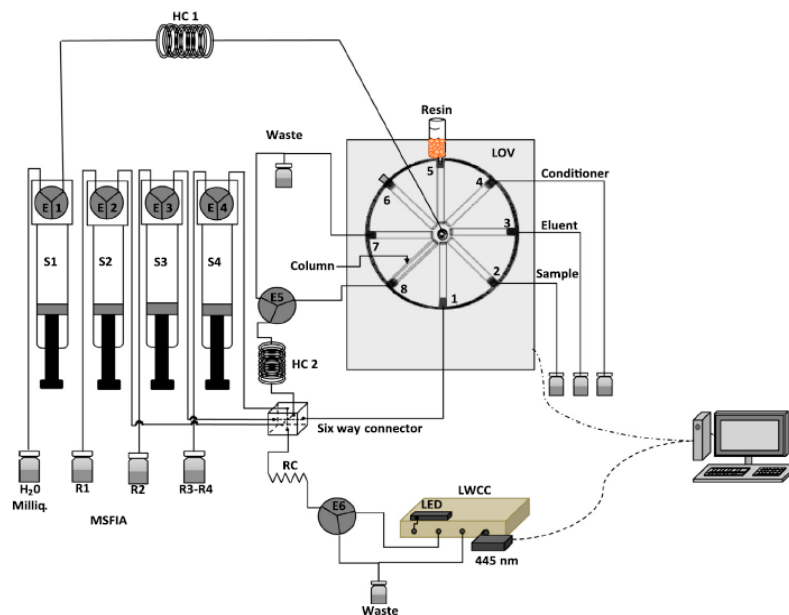
Fig. 1. Kinetic-catalytic MSFIA-LOV-LWCC-UV–vis system for manganese determination. LWCC: Liquid Waveguide Capillary Cell; HC: Holding Coils; RC: Reaction Coil; E: solenoid valves; S: glass syringes, R: reagent solutions.

programmable flow rate (MicroBU 16 A, Crison, Barcelona, Spain), a selection valve module (VA 2 SW, Crison) and an autosampler (Crison). The syringes S1, S2, S3 and S4 (Hamilton, Bonaduz, Switzerland) have the following capacities: 10, 1, 2.5 and 5 mL, respectively. Each syringe has a three-way solenoid valve on each head: E1, E2, E3, E4 (N-Research, Caldwell, NJ, USA). The "off" position (solenoid disable) of the valves connects syringes to a right channel and "on" position (solenoid enabled) to a left one. The MSFIA system has also two additional independent three-way solenoid valves (E5-E6) (Takasago, Electric INC, Tokyo, Japan). The syringe S1 is connected to a central port of the LOV through a holding coil (HC1), for loading and dispensing the liquids. Syringe S2 dispenses the hydrogen peroxide solution. The syringe S3 is employed to dispense tiron solution and syringe S4 contains the buffer-2,2-bypiridyl solution. Valve E5 is employed to connect the LOV with a second holding coil (HC2) or to the waste; E6 leads flow to

LWCC, which is connected to the spectrophotometer for the measurement, or to the waste. LOV is mounted atop of eight-position valve. Port 1 (P1) is connected to a six-way connector; port 2 (P2) is joined to the autosampler; ports 3 and 4 (P3 and P4) are for the eluent and conditioner, respectively; port 5 (P5) contain the reservoir of the resin; port 7 (P7) connects to the waste; port 8 (P8) is the microcolumn containing the resin and is coupled to the solenoid valve E5. Port 6 is not used. The manifold was built with PTFE (polytetrafluoroethylene) tubing of 0.8 mm i.d. to transport reagents and sample to the system, and 1.5 mm i.d. for picking up reagents. HC1 was constructed with 3 m of 1.5 mm i.d. PTFE tube, while HC2 and reaction coil (RC) with 3 m and 6 m long PTFE tube, respectively, of 0.8 mm i.d. A six-way connector of PMMA (polymethylmetacrylate) has been used for mixing reagents and sample and directing them to the reaction coil.

Instrumental control, acquisition and processing of data were performed using the software AutoAnalysis 5.0 (Sciware Systems, Bunyola, Spain).

2.4. Apparatus

A pH-meter Crison model 2002 was used for pH measurements. Spectrophotometric detection by means of a USB 2000 miniaturized CCD spectrophotometer (Ocean Optics), and a white super-bright LED light-source with variable intensity (Sciware Systems), was accomplished using a LWCC (World Precision Instruments, Inc., FL USA, Model 3100) of 100.0±0.5 cm optical length, internal volume 240 µL. The absorbance was measured at 445 nm with an integration time of 8 ms.

2.5. Procedure

The operational procedure for determining manganese is described in Table 1 and summarized as follows: the aspiration and injection of the reagents is given by syringe S1, which is connected to the central port of LOV by the holding coil HC1. As a first step, the resin is loading in microcolumn (P8). Then, resin is conditioned aspirating conditioning solution of 0.01 mol L^{-1} HNO_3 from P4 and injecting it through the resin, being directed to waste through the solenoid valve E5. Subsequently, the sample is aspirated from P2 and injected into the column and directed to waste. The elution of manganese is given aspirating 2.74 mol L^{-1} HNO_3 from P3, injecting through the column and directing to the holding coil HC2. Then a simultaneous injection of reagents is performed by activating the syringes S2 and S4 together with the eluate. Thus, the formed plug is mixed in the reaction coil (RC). Once the mixture is carried out, the plug is driven by Millipore water (P1) through the cell for subsequent detection at 445 nm.

2.6. Variable optimization

In order to achieve the most efficient performance in terms of highest analytical sensitivity and good repeatability, some experimental parameters were investigated.

Table 1
Automatic procedure for determination of manganese.

Description	Step	Volume (mL)	Flow rate (mL min^{-1})	Operation	Position of solenoid valves E1	E2	E3	E4	E5
Loop 1	1			Start: Sample change					
Multisyringe	2	1	10	Dispense	Off	Off	Off	Off	Off
Selection valve	3			Move to position 2					
Multisyringe	4	1	10	Pick up	On	Off	Off	Off	Off
Selection valve	5			Move to position 7					
Multisyringe	6	1.2	10	Dispense	On	Off	Off	Off	Off
Multisyringe	7	Fill		Pick up	Off	Off	Off	Off	Off
Loop 2	8			Start: for replicate					
Multisyringe	9	2.0	10	Dispense	Off	Off	Off	Off	Off
Selection valve	10			Move to position 4					
Multisyringe	11	2.0	10	Pick up	On	Off	Off	Off	Off
Selection valve	12			Move to position 8					
Multisyringe	13	2.0	2	Dispense	On	Off	Off	Off	Off
Selection valve	14			Move to position 2					
Multisyringe	15	1.5	10	Pick up	Off	Off	Off	Off	Off
Selection valve	16			Move to position 8					
Multisyringe	17	1.5	2	Dispense	On	Off	Off	Off	Off
Selection valve	18			Move to position 3					
Multisyringe	19	1.5	10	Pick up	On	Off	Off	Off	Off
Selection valve	20			Move to position 8					
Multisyringe	21	1.5	2	Dispense	On	Off	Off	On	On
Multisyringe	22	Fill		Pick up	Off	Off	Off	Off	Off
Multisyringe	23	1.5	2	Dispense	On	On	On	On	On
Ocean optics	24			Start Measure					
Multisyringe	25	3	2	Dispense	On	Off	Off	Off	Off
Ocean optics	26			Stop Measure					
Multisyringe	27	Fill	10	Priming	Off	Off	Off	Off	Off
Loop 2	28			End: repeat 3 times					
Autosampler	29			Position change					
Loop 1	30			End: repeat n times					

Since there were numerous variables to be optimized, and taking into account results of preliminary assays, variables were divided in two groups. Thus, the pH effect and the dispensing flow rates and volumes of sample and reagents were optimized by univariate approach. So, those conditions which provided the best response were established and therefore the interpretation of results was simplified.

For the second group, the optimization was carried out using a multivariate approach since it is an efficient tool in the process of optimizing analytical methods, allowing the simultaneous study of the relationship between responses and factors, and constructing a mathematical model through response surface methods. Firstly, a screening for four variables (hydrogen peroxide, tiron, buffer/bipyridyl and elution concentrations) was carried out applying a 2^k full factorial design in order to study the

effects of individual variables and their second order interactions. Finally, the critical values of the variables which affect significantly to the system were obtained by a face centered central composite design. Statistical calculations and experimental design have been performed by Statistica®.

3. Results and discussion

3.1. Analytical response

The net absorbance was determined as the absorbance of the Mn^{2+} standard/sample minus the absorbance of the blank, i.e. the reaction with lead (activator) without manganese using peak height as analytical signal.

Previous assays were performed for establishing the conditions of measurement and the effect of lead in the reaction in basic medium (Fig. 2). First, the action of the hydrogen peroxide on the oxidation of tiron in the presence of Pb^{2+} without manganese was performed at 445 nm, showing that there is no analytical signal of lead at this wavelength, as it has been previously reported [21].Then, the effect of oxidation of tiron by hydrogen peroxide in the presence of Mn^{2+} as the catalyst without Pb^{2+} was measured, resulting in a slow kinetic reaction for determination of Mn^{2+} and subsequently in a poor analytical signal. Finally, the effect of the hydrogen peroxide on the oxidation of tiron in the presence of Mn^{2+} and Pb^{2+} was measured giving a faster analytical response and also more sensitive. Therefore, the determination of Mn^{2+} was performed in the presence of Pb^{2+} as activator, since it did not affect the manganese quantification to the established wavelength.

Later the measurement mode, i.e. initial-rate mode and fixed time mode were tested in order to achieve the best ratio between Mn^{+2}/blank analytical signals. In the initial-rate mode, once the sample-reagent plug was into the LWCC, the flow was stopped and the analytical signal was registered each second up to reach a maximum slope value. In the case of fixed time mode, the absorbance measurements were made at maximum absorbance value. In terms of speed and sensitivity in the signal, the fixed time mode was selected as the best approach to carry out the proposed method.

3.2. Optimization of the variables

Based on previous works [8] ; [21], the effect of pH was examined over the range 9–10 by using 0.025 mol L^{-1} sodium tetraborate and adjusting with ammonia. The assays were carried out with 10 µg L^{-1} Mn^{2+} in 0.01 mol L^{-1} HNO_3, 0.2 mol L^{-1} of hydrogen peroxide, 0.01 mol L^{-1} tiron, 0.01 mol L^{-1} bipyridyl and 2 mol L^{-1} HNO_3 for elution. The maximum net absorbance obtained was with 0.05 mol L^{-1} concentration of borax.

The influence of dispensing flow rates for a simultaneous injection of sample, buffer-bipyridyl, hydrogen peroxide and tiron on the analytical signal was investigated within the range 1–2.3 mL min^{-1}. A flow rate of 2 mL min^{-1} for simultaneous injection of the four syringes was chosen for further experiments.

For the optimization of the volumes injected through the flow system, each reagent was tested for a range of 0.1–1.5 m L. Thus, combinations of these volumes for each reagent were injected into the system obtaining the maximum response for volumes of 0.37 mL tiron, 0.015 m L for hydrogen peroxide and 0.75 mL for buffer-

bipyridil.

To optimize the elution volume, 1, 1.5, 1.75 and 2 mL were studied. According to the percentage of recovery for manganese, the optimal volume of acid eluent was 1.5 mL. The optimal operation conditions are summarized in Table 2.

The optimization of reagents concentrations was studied by a multivariate approach. Firstly, a screening (2^k full factorial+3 central points) was performed, involving the following concentration variables (studied range in parentheses): bipyridyl (0.005–0.03 mol L^{-1}), hydrogen peroxide (0.2–0.4 mol L^{-1}), tiron (0.005–0.02 mol L^{-1}) and nitric acid for elution (0.7–3 mol L^{-1}). For these experiments a 10 µg L^{-1} of Mn^{2+} solution was used. The Pareto chart and the ANOVA table including curvature, significance of variables and pure error were evaluated. The factorial design demonstrated that the effects of bipiridil, hydrogen peroxide and elution solution concentrations were statistically significant in the studied experimental domain, while tiron concentration and their interactions with others variables did not show significant effects. So, the tiron concentration was fixed in 0.005 mol L^{-1}. Then, a face centered central composite design (CCD) was performed following the trends of the screening assays. Thus, the critical values of bipiridyl, hydrogen peroxide and nitric acid concentrations were established. In this case, ANOVA table, including curvature, significance of variables, pure error and lack of fit, histogram of residuals and the adjust coefficient of the selected model (linear/quadratic main effects+2 ways interactions) were evaluated. Critical values of 0.0195 mol L^{-1} for bipyridyl, 0.38 mol L^{-1} for H_2O_2, and 2.74 mol L^{-1} for nitric acid were used in further assays.
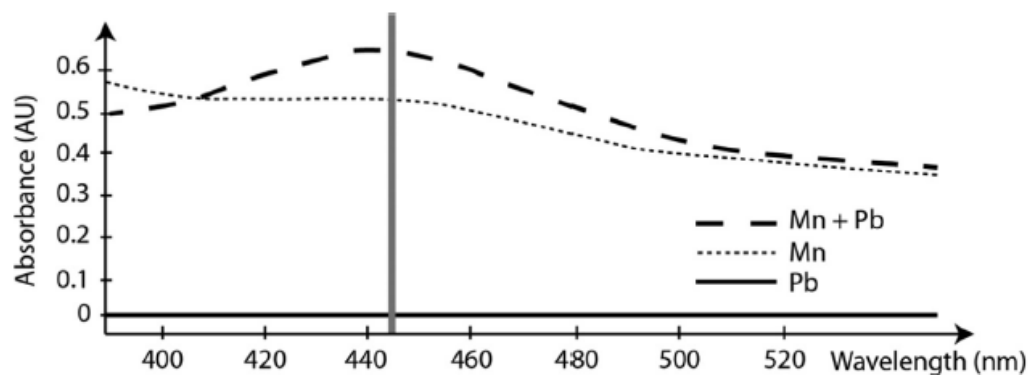
Fig. 2. Effect of the reaction of Mn^{2p} in presence of Pb^{2p} as activator.

Table 2
Optimized experimental conditions for manganese determination by MSFIA-LOV-LWCC-UV–vis system.

Operation conditions	
Flow rate of sample and reagents	$2\ mL\,min^{-1}$
Time on integration	8 ms
Sample coil	600 cm (1.5 mm i.d.)
Sample coil 2	21 cm (0.8 mm i.d.)
Reaction coil	600 cm (0.8 mm i.d.)
Sample volume	1.5 mL
Conditioner volume	2 mL
Elution volume	1.5 mL
Tiron volume	0.375 mL
H_2O_2 volume	0.150 mL
Buffer-2,2-Bipyridyl volume	0.750 mL
Tiron concentration	$0.005\ molL^{-1}$
2,2-Bipyridyl concentration	$0.0195\ molL^{-1}$
H_2O_2 concentration	$0.38\ molL^{-1}$
HNO_3 retention concentration	$0.01\ molL^{-1}$
HNO_3 elution concentration	$2.74\ molL^{-1}$
Buffer pH	10
Durability of resin	33 injections

3.3. Analytical parameters

The analytical parameters were evaluated under the optimal experimental conditions. The calibration curve for manganese determination was $y=(0.0318\pm0.0002)\,x+(0.00137\pm0.00005)$, (net absorbance vs. Mn^{2+} concentration in µg L^{-1}, $r^2=0.9999$, $n=8$). The detection limit (DL) was calculated from $3\sigma_b/S$, where σ_b is the blank standard deviation for ten replicates, and S is the slope of the calibration curve, while the quantification limit was calculated from $10\sigma_b/S$. Thus, the detection limit for manganese was 0.010 µg L^{-1} and the limit of quantification was 0.03 µg L^{-1}. The repeatability and reproducibility were expressed as relative standard deviation (RSD). The repeatability was evaluated from 10 successive injections of 15 µg L^{-1} of manganese, reaching a RSD of 1.4%. A reproducibility of 1.4% (RSD) was calculated from results obtained on different working days ($n=5$), using the same standard solution above-mentioned. Thus, the results obtained with the proposed system have a good level of precision. The injection frequency calculated for the developed method being 30 h^{-1} and the durability of the resin was 33 injections of seawater sample.

In Table 3, some of the main analytical features of the developed method and other methodologies for kinetic catalytic determination of Mn are summarized. The present work shows the major advantage in relation to detection limit, since it is between 75 and 1600 times lower than those reported in other methods, including FAAS detection systems [3]; [22]; [23] ; [24]. Moreover, our methodology does not require high sample volumes for a sample pre-concentration step to achieve the DL, while most of the methods needs higher volumes, even up to 100 ml of sample, only

a method uses 0.2 mL of sample but it reached a higher DL and also required strict control of temperature [3]. Moreover, the FAAS methods require a prior digestion of the sample. In addition, they are more expensive than the spectrophotometric ones.

Table 3
Main features of some recent studies on kinetic catalytic determination of manganese.

Detection with/without flow system	UV–vis	MCFIA-UV–vis	FAAS	FI-FAAS	MSFIA-LOV-UV–vis
Detection limit ($\mu g\,L^{-1}$)	16	6	0.75	12	0.010
Linear range ($\mu g\,L^{-1}$)	0–2058	25–1500	0.1–3.0	–	0.03–30
Type of sample	Marine pore wáter sample	Fresh and sea water	Natural water and food	Natural pond water	Marine and natural waters
Sample volume (mL)	0.2	10	25–100	15	1.5
Resin	–	EDTA/PbO$_2$	Zirconium (IV) hydroxide	Amberlite IRA-904	Dowex50 WX8
RSD (%)	1.3–4	2.6	7	2.2–3.1	1.4
Reference	[3]	[22]	[23]	[24]	Present work

Table 4
Tolerance limits for several ions on the determination of 15 mg L^{-1} manganese(II).

Ion added	Tolerance limit ($\mu g\,L^{-1}$)
K^+, Ca^{2+}	> 10 000
NO_3^-	2 000
Cr^{3+}	1200
Mo^{2+}, Al^{3+}, Ni^{2+}, Co^{2+}	1000
SO_4^{2-}, Cu^{2+}, Mg^{2+}	700
Cd^{2+}	500
Zn^{2+}	400
Fe^{2+}	200

Summarizing, in comparison with previous works, the proposed method presents a low limit of detection, good precision, wide working range and the sample does not require any pretreatment, allowing the directly introduction in the system.

3.4. Interferences

The effect of the presence of other ions on the trace determination of Mn^{2+} by the proposed method was studied. It has been assumed that an element does not interfere when the absorbance variation is lower than ±10%. For this purpose series

of solutions containing 15 µg L^{-1} of manganese were prepared, with the addition of potential interferents selected primarily for their presence in drinking and sea waters. The ions causing interference at low concentrations were Fe^{+2} and Zn^{+2} at 0.2 and 0.4 mg L^{-1}, respectively. The maximum tolerated concentration for each ion is shown on Table 4. These good results can be explained by the use of an on line sample clean-up procedure, since most of the potential interferences of the matrix were eliminated with the use of the Dowex resin, providing a high selectivity to the developed method.

3.5. Validation of the proposed methodology

The accuracy of the developed method was tested by the analysis of a certified reference material (CASS-4, seawater). This certified material was injected directly into the system, without pretreatment. The result obtained was compared (*t* test) with the given reference value and no significant differences at the 95% confidence level were found (Table 5). This shows that the MSFIA-LOV-UV–vis method can be successfully applied to manganese determination in complex matrices such as seawater. However, the analysis of other sample matrices could show better the grade of reliability of the method.

3.6. Analysis of natural water samples

The proposed analytical method was applied to the determination of manganese in different natural water samples with

Table 5
Analysis of certified reference material using the developed method.

Certified reference material CASS-4 (seawater)	Certified value	Obtained value[*]
Manganese ($\mu g\ L^{-1}$)	2.78 ± 0.19	$2.942 \pm 0.008\ (n=4)^a$

[a] Four replicates, and three peaks for each replicate.
[*] Standard deviation (SD) is calculated from cover factor k=2 (confidence in-terval 95%).

Table 6
Manganese determination in natural water samples.

		Mn	
Sample	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$) [a,b]	Recovery (%)
Seawater 1: Coastal area	0	1.5100 ± 0.0003	
	5	6.230 ± 0.011	94
Seawater 2: Harbor	0	0.8030 ± 0.0004	
	5	5.380 ± 0.013	92
Seawater 3: Open sea	0	0.9170 ± 0.0006	
	5	5.59 ± 0.005	93
Tapwater	0	2.7420 ± 0.0004	
	5	7.910 ± 0.007	104
Mineral water	0	1.3700 ± 0.0006	
	5	6.2200 ± 0.0005	97

[a] Results are expressed as mean of three determinations $\pm$ standard deviation
[b] Four replicates, and three peaks for each replicate.

satisfactory results. Three types of water matrices were analyzed, e.g. tap and mineral water, and seawater from harbor, open sea and coastal area. Four replicates were performed for each sample with and without spiking. The recoveries obtained for manganese ranged from 92–103% as shown in Table 6. The presence of manganese was found in all samples.

4. Conclusions

An automatic method was developed by coupling LOV and MSFIA flow analysis techniques with a LWCC exploiting UV–vis spectrophotometry detection. The manganese determination was based on the catalytic effect of Mn^{2+} on the oxidation of tiron, measured at a fixed time, since it allowed obtaining higher and rapid analytical signals than the initial-rate mode. Moreover, a low detection limit (DL) was achieved due to the use of a LWCC, because the light introduced into the

capillary is total and internally reflected to the detector. In addition, the potential interferences were eliminated by using Dowex resin for sample clean-up. Both, DL and direct analysis, together with the compactness (in comparison with atomic absorption spectrometers and conventional UV–vis laboratory instruments), become this method in an effective tool to determine Mn^{2+} *in situ*, per example to analyze seawater samples at shipboard.

The LOV-MSFIA-LWCC-UV–vis system provided significant advantages in precision and reproducibility, and high sample frequency. The proposed methodology was satisfactorily applied to a seawater certified reference material and natural water samples (seawater, tap and mineral water).

Acknowledgements

References

[1]   D.G. Marbaniang, Int. J. Environ. Prot. 2 (2012) 22–26.

[2]   M.P. Colombini, R. Fuoco, Talanta 30 (1983) 901–905.

[3]   J. Soto-Neira, Q. Zhu, R.C. Aller, Mar. Chem. 127 (2011) 56–63.

[4]   A.M. Aguilar-Islas, J.A. Resing, K.W. Bruland, Luminol. Oceanogr. Methods 4 (2006) 106–113.

[5]   D. Pérez-Bendito, M. Silva, Kinetic methods in analytical chemistry, in: Ellis Horwood (Ed.), Chichester, England, 1988.

[6]   H.M. Mottola, D. Perez-Bendito, Anal. Chem. 68 (1996) 257–289.

[7]   F. Grases, R. Forteza, J.G. March, V. Cerdà, Anal .Chim. Acta 155 (1983) 299–303.

[8]   E. Gómez, J.M. Estela, V. Cerdà, Anal. Chim. Acta 251 (1991) 305–311.

[9]   E. Gómez, J.M. Estela, V. Cerdà, J. Therm. Anal. 37 (1991) 195–202.

[10]   J.M. Estela, A. Caro, R. Forteza, V. Cerdà, Thermochim. Acta 200 (1992) 467–474.

[11]   Y. Ye, H. Mao, Y. Chen, Talanta 45 (1998) 1123–1129.

[12]   K. Mutaftchiev, Anal. Lett. 34 (2001) 1401–1411.

[13]   L. Su, J. Li, H. Ma, G. Tao, Anal. Chim. Acta 522 (2004) 281–288.

[14]   V. Cerdà, R. Forteza, J.M. Estela, Anal. Chim. Acta 600 (2007) 35–45.

[15]   V. Cerdà, J.M. Estela, R. Forteza, A. Cladera, E. Becerra, O. Altimira, P. Sitjar, Talanta 50 (1999) 695–705.

[16]   V. Cerdà, L. Ferrer, J. Avivar, A. Cerdà, Flow Analysis: A practical guide, Elsevier, Netherlands (2014), p. 278.

[17]   J. Ruzicka, E.H. Hansen, Trends Anal. Chem. 27 (2008) 390–393.

[18]   X. Long, E.H. Hansen, M. Miró, Talanta 66 (2005) 1326–1332.

[19]   J. Ruzicka, Analyst 125 (2000) 1053–1060.

[20]   L.J. Gimbert, P.J. Worsfold, Trends Anal. Chem. 26 (2007) 914–930.

[21]   L.J. Mallini, A.M. Shiller, Luminol. Oceangr. 38 (1993) 1290–1295.

[22]   S. Silva, J. Nóbrega, F. Rocha, Microchem. J. 98 (2011) 109–114.

[23]   D. Citak, M. Tuzen, M. Soylak, J. Harzadous Mater. (2010) 773–777.

[24]   M. Knap, K. Kilian, K. Pyrzynsk, Talanta 71 (2010) 406–410.