Contents lists available at ScienceDirect

Talanta

Automatic flow analysis method to determine traces of Mn^{2+} in sea and drinking waters by a kinetic catalytic process using LWCC-spectrophotometric detection

Laura Chaparro [a,b], Laura Ferrer [b], Luz O. Leal [a,*], Víctor Cerdà [b]

[a] Environment and Energy Department, Advanced Materials Research Center (CIMAV), Miguel de Cervantes 120, Chihuahua Chih, 31136, Mexico
[b] Department of Chemistry, University of the Balearic Islands, Cra.Valldemossa Km 7.5, E-07122 Palma de Mallorca, Spain

ARTICLE INFO

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 [7–10]. Some methods for the determination of Mn^{2+}

based on kinetic catalytic process have been reported in order to analyze waters samples [11–13]. 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 $1000\ \mu g\ L^{-1}$ stock solution (ultra pure, Scharlau, Barcelona, Spain) in $0.01\ mol\ L^{-1}$ of nitric acid.

Buffered reagent was prepared with borax ($Na_2B_4O_7 \cdot 10H_2O$) (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 $(NO_3)_2 \bullet 6H_2O$, 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
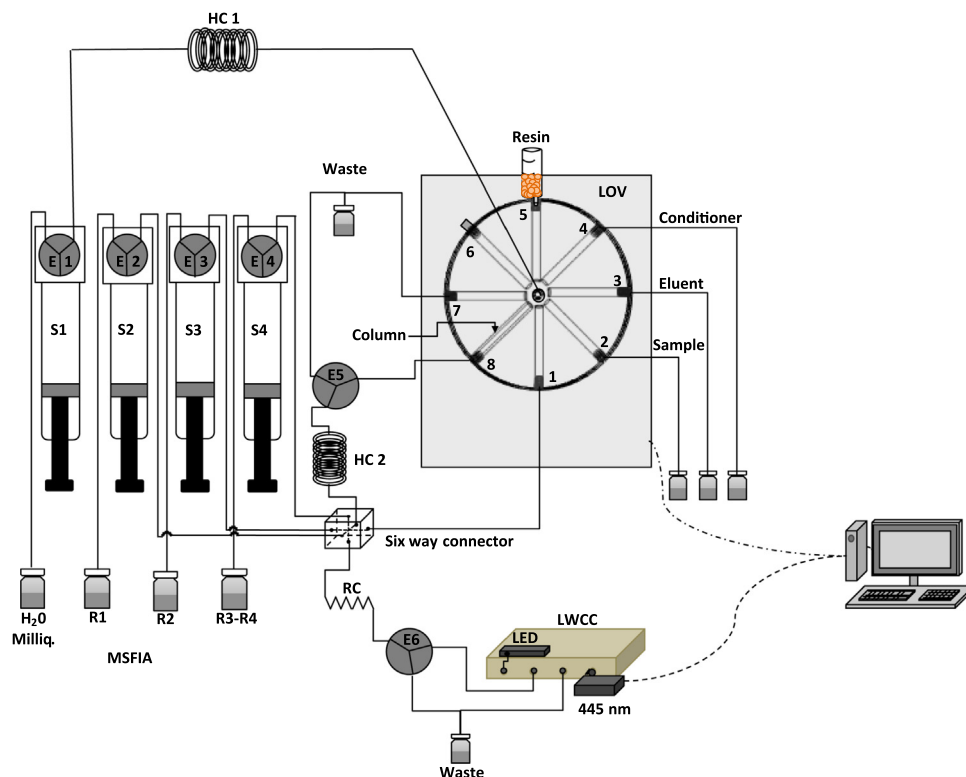

Fig. 1. Kinetic-catalytic MSFIA-LOV-LWCC-UV–vis system for manganese determination. LWCC: Liquid Waveguide Capillary Cell; HC: Holding Coils; RC: Reaction Coil; E: solenoid valves; S: glass syringes, R: reagent solutions.