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Development and application of a shipboard method for spectrophotometric determination of trace dissolved manganese in estuarine and coastal waters



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ABSTRACT

A shipboard method for the determination of trace dissolved manganese in estuarine and coastal waters was developed using a technique of reverse flow injection analysis, which adopted a 1-m liquid waveguide capillary cell and spectrophotometric detection of manganese derivation with 1-(2-pyridylazo)-2-naphthol (PAN). The design of dual-sample-carrier speeded up the sample throughput and eliminated the Schlieren effect. The salinity of estuarine and coastal waters caused a huge increase in the blank absorption value at the maximum absorption wavelength; therefore, a less sensitive detection wavelength was selected to achieve a low blank value while the method sensitivity was not significantly decreased. Method parameters were optimized. The salinity effect from estuarine and coastal waters was carefully investigated, and interference from iron was evaluated. The proposed method had high sensitivity with a detection limit of 3.0 nmol L^{-1} and a wide linear range of $10\text{--}1500 \text{ nmol L}^{-1}$ for dissolved manganese in seawater ($S=35$). The analytical results of five water samples with different salinities obtained using the proposed method showed good agreement with those using a reference ICP-MS method. The sample throughput of the proposed method was 120 h^{-1} , which was capable of obtaining high spatial and temporal resolution data in shipboard analysis. The proposed method had the advantages of convenient application in estuarine and coastal waters with different salinities, low detection limit, as well as high sample throughput. The proposed method was successfully applied to a 24 h on-line analysis and a shipboard underway analysis of dissolved manganese in the Jiulongjiang Estuary.

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1. Introduction

Manganese (Mn) is an essential micronutrient for marine phytoplankton growth, and is suggested to be a potentially (co-) limiting factor regulating primary production in high nutrient low chlorophyll regions (Middag et al., 2011; Twining and Baines, 2013). Dissolved Mn in seawater exists primarily as inorganic Mn (II), mainly in the forms of Mn^{2+} and MnCl^+ (Sunda et al., 1983). It is believed to serve as a useful chemical tracer in many estuarine and coastal processes, such as river plume dispersion, coastal inputs, benthic fluxes from sediments and anoxic/suboxic conditions. Influenced by a variety of hydrodynamic, physicochemical and biogeochemical processes, the behavior of dissolved Mn in estuarine and coastal waters is complicated. It can behave conservatively due to fast mixing processes and non-conservatively because of remineralization of organic material, removal at low

salinities and desorption from suspended particles (Colbert and McManus, 2005). The distribution of dissolved Mn in estuarine and coastal waters spans a large concentration gradient, typically from several nanomolar in the oceanic interface to several micromolar in the freshwater interface (Aguilar-Islas and Bruland, 2006; Roitz et al., 2002). Therefore, it is very important to accurately quantify the distribution of dissolved Mn in real-time with high spatial and temporal resolution for better understanding of estuarine and coastal processes and Mn biogeochemistry.

Among the existing methods commonly used for the determination of dissolved Mn in seawater, graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) are usually adopted. These methods need sample pretreatment with extraction/pre-concentration, such as solid phase extraction with various chelating resins and coprecipitation with magnesium hydroxide, to pre-concentrate the Mn ions and remove the seawater matrix (Biller and Bruland, 2012; Grotti et al., 2002). The land-based GFAAS and ICP-MS methods are sensitive, precise and accurate, yet obviously difficult to be applied to shipboard or *in-situ* analysis.

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Shipboard or *in-situ* methods based on flow injection (FI) technique have been developed in recent years. The FI system, which has the advantages of minimizing contamination and achieving high sample throughput and high precision measurement, has proved to be simple, robust, low-cost and appropriate in shipboard analysis of the oceanographic macronutrient elements (C, N and P) and micronutrient elements (Fe, Mn and others) (Hales et al., 2004; Li et al., 2013; Lohan et al., 2006; Worsfold et al., 2013). Combined with the FI system, methods based on chemiluminescence and catalytic spectrophotometry detection are already well studied and successfully applied to nanomolar Mn analysis in open ocean seawater (Aguilar-Islas et al., 2006; Doi et al., 2004; Mallini and Shiller, 1993; Okamura et al., 2001; Resing and Mottl, 1992). These methods can reach a very low detection limit, but the detection signal can be severely affected by pH, reaction temperature and sample matrix/salinity effect. Therefore, skillful and careful operation and extraction/pre-concentration technologies are still necessary; moreover, the large salinity and Mn concentration gradient and high concentrations of dissolved organic matter (DOM) in estuarine and coastal waters limit the application of these methods.

Colorimetric FI methods based on the spectrophotometric detection of the 1-(2-pyridylazo)-2-naphthol (PAN)-Mn complex have been developed and applied to *in-situ* Mn analysis in coastal and hydrothermal plume waters (Chin et al., 1994, 1992; Statham et al., 2005, 2003). However, the detection limit of these methods (20 nmol L^{-1}) is not low enough to accurately quantify the low Mn concentrations in the oceanic interface of estuarine and coastal waters. In addition to extraction/pre-concentration methods, increasing the optical path length of the measurement cells by means of liquid waveguide capillary cell (LWCC) devices is also an effective approach to enhance the sensitivity of conventional spectrophotometry (Páscoa et al., 2012; Zhang, 2006). The light introduced to the LWCC is totally internally reflected at the interface between the tubing made of a flexible fluoropolymer material (Teflon AF, DuPont) with a refractive index (1.29) and a liquid medium with a higher refractive index (water, 1.33; seawater, 1.34), and passes through the capillary to a detector (Gimbert and Worsfold, 2007). Therefore, a long optical path length is provided, resulting in an enhancement of sensitivity for the spectrophotometric method and thus an improvement of the detection limit.

The basic mode of flow injection analysis (FIA), which involves injection of a discrete sample zone into a continuously flowing stream of carrier or reagent, is known as normal flow injection analysis (nFIA). In reverse flow injection analysis (rFIA), with the injection of reagent into a continuously flowing stream of the sample, the sample dispersion is lessened; and higher analytical sensitivity and lower reagent consumption can be obtained (Mansour and Danielson, 2012). In addition, in rFIA, the sample can behave as a washing solution, which to a large extent eliminates the carryover effect. Since the consumption of reagent is minimized, rFIA is more suitable for shipboard and long term observations. Combined with LWCC and a spectrophotometric detector, rFIA has been successfully applied to the determination of nanomolar soluble reactive phosphorus (Ma et al., 2009), nitrite and nitrate in seawater (Feng et al., 2013) and iron in rainwater (Huang et al., 2009).

The use of rFIA with a LWCC for determination of Mn in natural waters has not yet been reported. In this study, for the purpose of exploring a suitable technique for shipboard monitoring of dissolved Mn in estuarine and coastal waters, a simple rFIA-LWCC system coupled with the spectrophotometric detection of the PAN-Mn complex was developed. The detected Mn species is expected to be primarily dissolved Mn (II), and may contain some labile colloidal Mn (Statham et al., 2005). The data are reported as

operationally defined dissolved Mn (dMn). The large variation of salinity in estuarine and coastal waters is one of the primary problems hindering the application of spectrophotometric analytical methods; and so, the effects of varying salinity were studied. Experimental parameters were optimized to achieve satisfactory sensitivity and precision. The proposed method was applied to a 24 h on-line and an underway analysis of dMn in estuarine and coastal waters in Wuyuan Bay (Xiamen) and the Jiulongjiang Estuary, and the distributions of dMn in the surface water of these areas were reported.

2. Experimental

2.1. Reagents and solutions

All reagents and standards were prepared in a Class-100 laminar flow bench using ultra-pure water ($18.20 \text{ M}\Omega \text{ cm}$) obtained from a Millipore Purification Water System (Millipore Co., USA). Plastic ware for storing reagent solutions and standards as well as water samples was low-density and high-density polyethylene (Nalgene, USA) and washed following the procedure of Achterberg et al. (2001).

Borate buffer solution was prepared by dissolving 1.236 g H_3BO_3 (EMSURE[®], Merck, Germany) in 200 mL 0.1 mol L^{-1} NaOH (GR, Shanghai Shanhai Gongxuetuan No. 2 Experiment Factory, China) solution. PAN stock solution (0.8 mmol L^{-1}) was prepared by mixing 0.05 g PAN (Merck, Germany) and 5 mL Triton X-100 (laboratory grade, Sigma-Aldrich, USA) into 50 mL ultra-pure water. Stirred with a magnetic stir bar and heated to $80 \text{ }^\circ\text{C}$, PAN could be totally dissolved in 8 h (Chin et al., 1992). The PAN mixed solution was prepared by mixing 1.0 mL PAN stock solution with 40 mL borate buffer solution, and brought up to 100 mL with ultra-pure water. The final pH of the PAN mixed solution was approximately 10.0 ± 0.1 .

Mn standard solutions were prepared using appropriate dilution of commercial atomic absorption standard solution ($1000 \mu\text{g mL}^{-1}$, Fluke, USA) in ultra-pure water or low Mn seawater (LMSW, salinity approx. 35) which had an Mn concentration below the detection limit, and was collected from the surface of the South China Sea using a towed fish underway sampling system (Huang et al., 2012).

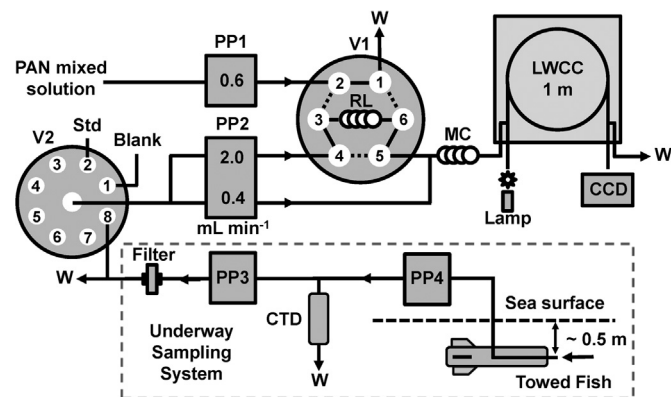


Fig. 1. Configuration of detection manifold and underway sampling system. PP1–PP4, peristaltic pumps; V1, 6-port, 2-position injection valve; V2, 8-position selector valve; MC, mixing coil, 10 cm; RL, reagent loop, 20 cm (injection volume, 88 μL); CCD, variable wavelength spectrophotometer; Std, standard solution; W, waste; the solid line of V1 represents the valve at position A, and the dashed line represents position B.

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