



Original article

Iodide analysis by ion chromatography on a new stationary phase of polystyrene-divinylbenzene agglomerated with polymerized-epichlorohydrin-dimethylamine



Mu-Hua Wang^{a,*}, Zhong-Ping Huang^{b,c}, Jun-Wei Liu^b, Jie He^b, Jia-Jie Zhang^b, Yan Zhu^{b,*}

^a Department of Chemistry, Lishui University, Lishui 323000, China

^b Department of Chemistry, Xixi Campus, Zhejiang University, Hangzhou 310028, China

^c College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, China

ARTICLE INFO

Article history:

Received 29 December 2014

Received in revised form 20 March 2015

Accepted 14 April 2015

Available online 11 May 2015

Keywords:

PEPI-DMA

Stationary phase

DC amperometric detector

Iodide

Povidone iodine solution

Kelp

ABSTRACT

A new stationary phase for iodide ion analysis has been developed. The cationic polymer-epichlorohydrin-dimethylamine (PEPI-DMA) was served as modifier in synthesizing polyelectrolyte sorbents and the macroporous polystyrene-divinylbenzene (PS-DVB) resin was used as support. The positively charged polymer (PEPI-DMA) was electrostatically bonded to a negatively charged particle (PS-DVB sulfonated). The new stationary phase was characterized by scanning electron microscopy (SEM), Fourier transform infrared (FTIR), elemental analysis, chemical adsorption and desorption measurements. The chromatographic evaluation of the new stationary phase was performed using various anions with a conductivity detector. The new stationary phase was also applied to the determination of iodide directly with a DC amperometric detector using a platinum working electrode and an Ag/AgCl reference electrode. The chromatographic conditions were optimized and the eluent solution contained 5 mmol/L HNO₃ and 15 mmol/L NaNO₃ at a flow rate of 1.0 mL/min and column temperature of 30 °C. The applied voltage of the DC amperometric detector was 0.9 V. Under the optimum conditions, the linear range of the method was 0.2–50 mg/L for iodide ion with a correlation coefficient of 0.9990. The detection limit was 0.05 mg/L (calculated at S/N = 3) and the relative standard deviations (RSD, *n* = 6) were all less than 1% for retention time, peak area and peak height. This method was also utilized for the determination of iodide ions in samples of povidone iodine solution and kelp samples with satisfactory results.

© 2015 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Over the past three decades, ion chromatography (IC) has blossomed into an excellent tool for the analysis of charged species such as inorganic ions and small ionizable molecules. With the same principles as HPLC, the stationary phase plays a very important role in the process of ion chromatographic separation. Therefore, developing a new stationary phase is extremely beneficial (necessary) and meaningful [1,2]. In IC, the stationary phase mainly consists of silica-based and polymer-based exchangers [3,4]. Silica-based exchangers [5–7] are rigid, but have a limitation in their operating pH range because the silica backbone

is unstable at pH < 2 and pH > 8. Polymer-based columns are more commonly used in IC due to tolerance to high pH eluents. Polystyrene-divinylbenzene (PS-DVB) copolymer anion exchangers [3,8] are commonly used for anion separation by IC. The methods of preparation of stationary phases includes surface-grafted [9–12], surface-embedded and surface-agglomerated [3,13–16]. Agglomerated anion exchange phases consist of a polymer core bearing sulfonic acid groups with an agglomerated layer of nanometer-sized polymer particles (latex) functionalized with alkyl quaternary ammonium groups [17,18]. This approach of stationary phase preparation provides a number of significant advantages including compatibility with pH 0–14 of the mobile phase when the particles are prepared with styrene based monomers and excellent long-term chemical stability in order to provide long-term consistency of stationary phase selectivity [3]. However, the polymeric phases have lower thermal and mechanical stability, and lower efficiencies compared with

* Corresponding authors.

E-mail addresses: lsxywmh@126.com (M.-H. Wang), zhuyan@zju.edu.cn (Y. Zhu).

inorganic oxides such as silica and zirconia [19]. Therefore, the development of new stationary phases continues to be one of the most challenging research goals in IC.

Alkyl quaternary ammonium groups are commonly used as modifiers of a cation-exchange chromatographic stationary phase. Poly-epichlorohydrin-dimethylamine (PEPI-DMA), which is an effectively water-soluble cationic polyelectrolyte with amidocyanogen and ammonium ion, has been applied in the treatment of printing and dyeing wastewater [20–24]. In this paper, a polystyrene-divinylbenzene stationary phase agglomerated with PEPI-DMA for IC was synthesized and studied.

Iodine is an essential element for human beings. The lack of iodine leads to iodine deficiency disorder (IDD), while excessive dietary intake of iodine can result in serious pathological problems [25,26]. A number of analytical methods have been developed for the determination of iodide in seawater [27,28], povidone iodine solution [26], urine [29], edible seaweed [25], and other samples [30,31]. Also, the determination of iodide directly, or indirectly, has been accomplished by catalytic spectrophotometry [25], IC with columns and column-switching technique [26], HPLC with pulsed amperometric detector [29], electrostatic ion chromatography [28], polymeric membrane sensors [30], flow injection [32], capillary electrophoresis [27], and gas chromatography–mass spectrometry after derivatization [33]. However, the pretreatment processes required and the analytical processes of samples are complex in the methods above. The method described in this paper is based on a new homemade stationary phase which was successfully applied to the determination of iodide in povidone iodine solutions and kelp samples directly and conveniently.

2. Experimental

2.1. Equipment

The chromatographic system consisted of an DX-120 ion chromatograph (DIONEX, Sunnyvale, CA) with a dual-piston serial pump, a Rheodyne (Cotati, CA, USA) six-port valve, a 25- μ L sampling loop, a conductivity detector or an ED40 electrochemical detector equipped with a platinum working electrode and an Ag/AgCl reference electrode. Chromeleon 6.8 chromatography data management software (Thermo Scientific, Sunnyvale, CA, USA) was used for system control and data processing. The voltage parameter for the DC amperometric detector was 0.90 V. The eluent contained 5 mmol/L HNO_3 and 15 mmol/L NaNO_3 with a flow rate 1.0 mL/min. The packing system consisted of a nitrogen cylinder, a pneumatic pump, a slurry reservoir, jointing units, and stainless-steel analytical columns.

2.2. Reagents

The 1,2-diaminoethane was purchased from Aladdin Chemical Co., Ltd. (Shanghai, China). Dimethylamine (DMA, 33% in H_2O , v/v), epichlorohydrin (EP), ethanol, nitric acid, sodium nitrate, potassium iodide, sulfuric acid, glacial acetic acid and dichloromethane were purchased from Huipu Chemical Reagent Co., Ltd. (Hangzhou, China).

Polystyrene-divinylbenzene (PS-DVB) substrate beads were synthesized according to the literature [24]. A water purification system (Millipore, Milford, MA, USA) was used to further deionize distilled water for all eluents and sample mixtures. Standard solutions of F^- , Cl^- , Br^- , NO_2^- , NO_3^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, I^- and SCN^- ions were prepared by diluting the stock solutions to required concentration just prior to use. Other chemicals were used as received.

2.3. Sample treatment

The sample of povidone iodine solution was produced by dissolving the proper amount of povidone iodine solution in 100 mL deionized water, and filtered through a 0.22 μm membrane filter and SPE-C18 column (Tianjin Fuji Science & Technology Co. Ltd., Tianjin, China) before injection.

The sample of kelp was randomly bought at a local market. The treatment process was as follows: Firstly, the sample, after removal of sediment, was chopped up and dried at 60 $^\circ\text{C}$ and then the sample was milled and accurately weighed in 50 mL deionized water, then subjected to ultrasonification for 1 h. Finally the sample was mixed thoroughly before centrifuging for 20 min at 12,000 rpm, and the supernatant solution was filtered through a 0.22 μm membrane and SPE-C18 column before injection. The first 1 mL of eluate was discarded and the following solution was collected for further analysis.

2.4. Preparation of anion exchange column

2.4.1. Synthesis of PEPI-DMA

The synthesis procedure of PEPI-DMA was according to the literature [34] and the reaction equation is shown in Fig. 1. Specifically, the polymerization was carried out in an ethanol solution as follows: Dimethylamine (13.66 g) was first added to a 250 mL glass reactor equipped with a temperature controller at 0 $^\circ\text{C}$ initially with a magnetic stirrer, then, cold epichlorohydrin (13.88 g) at a dimethylamine to epichlorohydrin molar ratio (1:1.5) was added dropwise into the reactor with constant stirring to form oligomers. Next, 1,2-diaminoethane at a chosen weight percentage (3%) of the mixture was added dropwise into the reactor under stirring and then, the reactive temperature was raised slowly to 70 $^\circ\text{C}$. The polyamine polymers were finally obtained after 7 h reaction.

2.4.2. Preparation of anion-exchange stationary phases with PEPI-DMA

The synthesis procedure of PS-DVB and sulfonated PS-DVB has been reported previously [26]. An aqueous solution of PEPI-DMA was added to another aqueous suspension of sulfonated PS-DVB, the reaction mixture was stirred at 70 $^\circ\text{C}$ for 2 h.

2.4.3. Column packing procedure

The column was packed by a slurry packing technique. A 3.0 g of slurry of PEPI-DMA agglomerated PS-DVB beads was dispersed into 60 mL of deionized water and sonicated in an ultrasonicator for 10 min and then pressed into an empty column (stn stl, 200 mm \times 4.0 mm, id), with deionized water as packing solvent at a working pressure of 3000 psi. The volume of packing solvent passing through the column should be at least 400 mL. The

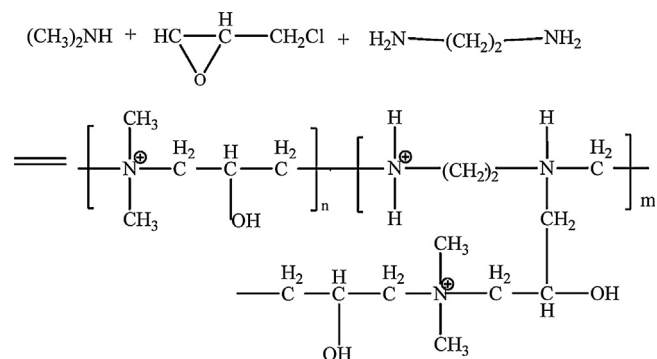


Fig. 1. The reaction equation of PEPI-DMA.

Download English Version:

<https://daneshyari.com/en/article/1257223>

Download Persian Version:

<https://daneshyari.com/article/1257223>

[Daneshyari.com](https://daneshyari.com)