



# Large volume preconcentration and determination of nanomolar concentrations of iron in seawater using a renewable cellulose 8-hydroquinoline sorbent microcolumn and universal approach of post-column eluate utilization in a Lab-on-Valve system



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## ARTICLE INFO

### Article history:

Received 13 October 2015

Received in revised form

14 December 2015

Accepted 16 December 2015

Available online 18 December 2015

### Keywords:

Lab-on-Valve

Bead injection

8-Hydroquinoline-modified cellulose sorbent

Iron determination in seawater

1

10-Phenanthroline

Long-path detection cell

## ABSTRACT

We report on a Lab-On-Valve (LOV) configuration for analyte preconcentration from milliliter sample volumes using confluent mixing in the holding coil for in-line addition of loading buffer. The system was applied to the spectrophotometric determination of iron(II) in acidified seawater using 1,10-phenanthroline as color reagent. A cellulose-based chelating sorbent containing 8-hydroxyquinoline was used for the first time in LOV and excellent retention behavior and loading capacity were found.

The flow system employs a syringe pump for handling all solutions (sorbent suspension, loading buffer, water, eluent, and color reagent) and a peristaltic pump for sample propulsion and includes a fit-for-purpose 14 cm long detection glass flow cell and a bubble trap for in-line carrier degasification.

Advantage was taken of the LOV flow-through port to keep the eluted analytes for re-aspiration for subsequent chromogenic reaction. In effect, a universal analyzer configuration and preconcentration procedure was developed, which is combinable with other analytes, sorbents, and reagents.

Among the studied parameters were the compositions, pH, volumes, and flow rates of loading buffer, eluent, and color reagent, as well as the microcolumn size, repeatability, and system stability.

Reproducibility of 4.1% RSD over the entire working range, a LOD of down to  $5 \text{ nmol L}^{-1}$ , sampling frequency of  $12 \text{ h}^{-1}$ , and linearity up to  $1 \text{ } \mu\text{mol L}^{-1}$  for 3.3 mL of sample were obtained and applicability to real samples was demonstrated. It was proven that both Fe(III) and Fe(II) were retained and yielded similar recovery and sensitivity values. The method was applied to coastal seawater samples and spiking experiments yielded recovery values close to 100%.

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## 1. Introduction

The development of new preconcentration methods, study of new solid phase extraction (SPE) sorbents, and the possibility of hyphenation and automation of preconcentration and analysis especially for traces of transition metals are key tasks for chemical oceanographic research [1,2].

SPE is one of the most-frequently used sample preparation techniques in analytical chemistry with special importance for environmental monitoring and research due to the ability to eliminate sample matrix simultaneously to analyte preconcentration.

Manual operation of SPE is feasible with high recovery and sample throughput as numerous samples can be treated

simultaneously. Straightforward handling, reasonable price, and disposable SPE cartridges are worthy advantages especially in food or clinical analysis.

However, when used for preconcentration of transition metal cations at nanomolar concentration level with possible contamination during sample treatment from the laboratory environment, automation of the SPE procedure in a closed system presents a superior approach of operation. Therefore, in oceanographic research of the sources, distribution, and sinks of transition metals, SPE procedures are mostly automated such as by Flow Injection Analysis (FIA) [3], Sequential Injection Analysis (SIA) [4,5], or other derived flow analysis techniques (FA) [6,7] in a closed manifold.

Of special interest is the capability and efficiency of FA for the automation of both SPE-based analyte preconcentration and quantification in one single procedure. Vice versa, SPE allows to improve the selectivity and sensitivity of automated trace metal determinations significantly [8,9].

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Development and successful application of portable flow-based systems have been reported for shipboard operation [10–18]. An important benefit of obtaining the analytical result shortly after sampling is the possibility of assessment whether renewed sampling is required for result confirmation or if a further exploration of the sample side is of interest. Online measurements in a continuous sample flow for surface water mapping [19] and recently in-situ measurement enabling real-time depth profiling [20] using FA-based analyzer systems have been reported.

For SPE in FA, cartridges, pre-filled with a chelating resin, are typically used as preconcentration columns. This approach is beneficial for costly sorbents but bears the potential of blockage or increasing backpressure by column compaction and loss of comparability if the column has to be refilled. When sample loading is done by peristaltic pumps or by gas-pressure [9,21], an increase of backpressure can cause a decrease of the loaded sample volume and loss of accuracy.

In-system packing of a micro-column from a suspension of sorbent particles or “beads” was therefore a milestone invention in FA and is known as Bead-Injection (BI) [22,23]. It is generally automated by the FA platform “Lab-on-Valve” (LOV) [24] with comprehensive reviews found elsewhere [25,26].

While based on principally the same instrumentation as SIA, LOV takes advantage of an especially designed valve stator (LOV manifold) to miniaturize SIA protocols and to facilitate monitoring applications (integration of a flow-through port).

Reproducible creation of microcolumns from sorbent suspension is straightforward by smooth and straight flow channels for easier handling and packing the sorbents beads. Packing and renewal of a microcolumn of only a few milligram of sorbent is done in an automated and reproducible fashion. This miniaturized SPE is attractive even with costly sorbent materials as typically used for trace metal enrichment.

LOV has been used for preconcentration of transition metals combined e.g. with online-coupled GFAAS [27–29], atomic fluorescence [30,31] or using off-line analysis with ICP-MS [21,26]. Only few works reported on metal preconcentration including in-LOV optical detection [32,33]. An important reason is that due to the principle of miniaturization and the single-channel character of LOV (one pumping and reaction line), SPE and posterior mixing with a color reagent are difficult to perform “on-LOV”. Benefit of the integrated multipurpose detection cell of the LOV can be taken if color reaction and quantification is performed “on-sorbent” or using the color reagent in the eluent. However, in the first case, a transparent and suitable sorbent has to be packed with high reproducibility in the detection cell and transferability to different analytes is questionable. In the second case, the compatibility of elution conditions and color development must be fulfilled. In consequence, post-SPE chemical reactions are performed rather outside the LOV manifold employing additional pumps for reagent confluence to the eluate [34].

Even without SPE preconcentration, highly sensitive assays based on FA for transition metals in seawater have been reported using chemiluminescence [35], fluorescence detection [36], or long-waveguide capillary detection cell (LWCC) [15,16]. Use of a syringe pump (SP) for precise solution handling rather than peristaltic pumps (PP) ensures for a high pressure stability and volumetric reliability over time.

For preservation, seawater samples for transition metal analysis are acidified generally to pH 1.7. Continuous pumping (e.g. in FIA by PP) reveals here an advantage over SIA/LOV because buffer addition (for optimal loading pH) can be done by confluence to the sample. This in turn allows large volume preconcentration of e.g. iron as the analyte of interest in this work [10–12,14,17–19,37–40].

Using SIA or LOV, either off-line buffering or alternating aspiration of buffer and sample are required if preconcentration of

large sample volumes is strived for. On the other hand, direct load of acidified seawater has been demonstrated using NTA superflow resin [13].

In cases where element selective detection such as GFAAS is not available, FA systems are generally designed for the determination of one element only, e.g. by a selective chromogenic reaction. Elution and reagent addition are often done in a single step. This implies that the conditions and eluent have to be adapted for each analyte, thus presenting a loss of the system's versatility.

In this work, this limitation was overcome by a new LOV arrangement with an on-demand renewable SPE microcolumn using one PP for a continuous flow of sample plus one SP for confluence of a loading buffer already in the holding coil and prior to sample load. By this, a lasting aspiration of sample prior to loading was not required. Using the flow-through port of the LOV, the analyzer design allows keeping the eluate for posterior mixture with the color reagent. By this, SPE and analytical reaction are independent. No external vial for elute collection is needed, by this avoiding the risk of contamination or carry-over and required post-analysis cleaning.

Iron was chosen as an analyte of special interest in oceanography as it acts in different regions of the world oceans as a limitation factor for algal growth [41,42]. Its analysis is therefore of high concern as reflected in two reviews [42,43]. Moreover, iron(II) forms relative weak complexes and an efficient preconcentration protocol will be applicable to other transition metals as well. It is also a ubiquitous element so contamination is likely and new approaches to its reliable analysis are of importance.

Consequently, a portable analyzer and robust method for the preconcentration and analysis of iron(II) based on BI, potentially applicable to other analytes and detection techniques would be a valid contribution to chemical oceanographic research.

Apart from element selective detection systems such as ICP-MS [21,44,45] or GFAAS [13,40], most commonly employed for iron analysis are specific chromogenic reagents 1,10-phenanthroline and ferrozine [15,16,20,39] or more sensitive catalytic assays based on oxidations of either luminol with chemiluminescence detection [10–12,17,19,35,37,38] or of *n,n*-dimethyl-*p*-phenylenediamine with spectrophotometric quantification [11,13,14,18]. In this work, spectrophotometric detection of the iron(II)-1,10-phenanthroline complex was done as a simple approach to study the sorbent behavior while the analyzer allows universal post-elution use of the eluent such as for ion-chromatography.

Use of cellulose sorbent particles for BI in a LOV analyzer was studied for the first time as a relatively new, economic, hydrophilic, and over a wide pH-range stable sorbent material [46]. The work included the optimization of bead handling and study of different functionalities. The best one was then used to develop an automated method for large volume SPE with the objective of high system robustness, time stability, and simple renewal of the SPE microcolumn.

## 2. Material and methods

### 2.1. Reagents and solutions

Ultrapure water (18.2 M $\Omega$  cm) delivered by a Millipore system was used throughout. All glass and plastic ware was cleaned with 10 mmol L<sup>-1</sup> hydrochloric acid directly before use. All reagents were purchased from Sigma Aldrich (Prague, Czech Republic) if not stated otherwise.

Four cellulose based sorbents from Iontosorb (Usti nad Labem, Czech Republic) of 50–80  $\mu$ m particle diameter (particle porosity 100, capacity 0.2 mmol/g) and the following functionalities were tested: diethylenetriamine (DETA), diethylene-triamine-tetraacetic

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