Fast direct determination of strontium in seawater using high-performance chelation ion chromatography

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ABSTRACT

A new method for the fast direct chromatographic determination of strontium in seawater has been developed. Two coupled silica monolithic columns (total dimensions 200×4.6 mm I.D.) chemically modified with iminodiacetic acid (IDA) functional groups were used for baseline separation of all alkaline-earth metals in seawater in less than 4 min at flow rate of 4.0 mL min^{-1}, using an eluent containing 0.25 M sodium chloride and 2 mM glycolic acid, pH 5.11. Several colour-forming ligands, including o-cresolphthalein complexone (o-CPC), methylthymol blue (MTB), xylenol orange (XO), 4-(2-pyridylazo)resorcinol (PAR) and ZnEDTA–PAR were evaluated as reagents for post-column reaction (PCR) based spectrophotometric detection. Sensitivity of the developed method for strontium was at the low mg L^{-1} level in undiluted seawater samples, in the presence of excessive amounts of calcium and magnesium, using post-column reaction detection with o-CPC at 570 nm. The method allowed quantitative determination of strontium in seawater samples (LOD 3.23 ± 0.15 mg L^{-1}, $s_r = 4.6\%$), with direct injection of just 4 μL of seawater onto the chromatographic column.

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1. Introduction

Determination of alkaline-earth metal cations in seawater is of great importance for marine science and various environmental studies. For example, there is considerable demand for methods enabling the monitoring of Mg^{2+}, Ca^{2+} and Sr^{2+} ion concentrations in seawater as a part of coral skeleton growth and calcification studies [1] following the effects of seawater acidity with variations in ocean temperatures. However, seawater has been recognised as one of the most difficult matrices for direct analysis of metal ions due to its high salinity and incommensurable levels of analyte and matrix ions. At present, it is a routine practice in marine science and, especially in research on coral skeleton growth, to determine changes in Mg^{2+}/Ca^{2+} [2] and Sr^{2+}/Ca^{2+} concentration ratios [3] rather than to measure accurately the absolute concentrations of these elements. Having said this, it is clear that determination of the exact concentration levels of these elements in seawater is an important goal, providing accurate data for the correct interpretation and modelling of numerous biochemical processes in seawater.

The number of suitable methods for the direct (undiluted) determination of strontium in seawater is limited, most providing rather low precision and accuracy, as a result of the complexity and high ionic strength of seawater as a sample matrix. The majority of current methods, including atomic absorption spectroscopy (AAS) [4], flame

photometry [5], and neutron activation analysis (NAA) [6] were developed in the later half of last century, and have changed little since that time. The suitability of these methods for the analysis of large numbers of seawater samples is also questionable, due to issues related to salt build-up and precipitation [4,7,8]. For example, the officially recommended AAS protocol "ASTM D3352-08a Standard Test Method for Determination of Strontium Ion in Brackish Water, Seawater, and Brines", covers the concentration range of 5–2100 mg L^{-1} strontium [9]. According to this method, the procedure requires some sample preparation including the dilution of seawater samples and the addition of the releasing agent lanthanum, to minimise the chemical interferences from the other components of seawater, such as sulphate and phosphate.

It should be noted that suitability of inductively coupled plasma mass spectrometry (ICP-MS) to the determination of strontium in seawater is also limited, in the first instance by a strong interference of calcium dimer ions, and secondly by analysis cost. Strontium has four naturally occurring stable isotopes, ^{84}Sr, ^{86}Sr, ^{87}Sr, and ^{88}Sr, with abundances of 0.56, 9.87, 7.04, and 82.53 at.%, respectively, and calcium in nature is presented by six isotopes, ^{40}Ca, ^{42}Ca, ^{43}Ca, ^{44}Ca, ^{46}Ca, and ^{48}Ca, with abundances of 96.95, 0.65, 0.14, 2.086, 0.004, and 0.19 at.%, respectively. So, the signal from Ca-dimer ions ($^{40}Ca^{44}Ca^+$, $^{42}Ca_2^+$, $^{40}Ca^{46}Ca^+$, $^{42}Ca^{44}Ca^+$, $^{43}Ca_2^+$, $^{40}Ca^{48}Ca^+$, $^{42}Ca^{46}Ca^+$, $^{44}Ca_2^+$) results in isobaric interferences on Sr ($^{84}Sr^+$, $^{86}Sr^+$ and $^{88}Sr^+$) signals. The isobaric interference of molecular ions or Ca-argides ($^{36}Ar^{48}Ca^+$, $^{38}Ar^{46}Ca^+$, $^{40}Ar^{44}Ca^+$, $^{38}Ar^{48}Ca^+$, $^{40}Ar^{46}Ca^+$, $^{40}Ar^{48}Ca^+$) should be also taken into consideration for the ICP-MS determination of strontium

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and calcium [10]. Rubidium has two naturally occurring stable isotopes ^{85}Rb and ^{87}Rb, with abundances of 72.17 and 27.83 at.%, respectively. The concentration of Rb in seawater is about 0.12 mg L^{-1} and there is isobaric interference of the signal from ^{87}Rb$^+$ on the ^{87}Sr signal. Interference correction both in multi-collector ICP-MS and in thermal ionisation mass spectrometry (TI-MS) modes requires chromatographic separation of strontium from calcium and rubidium. For this purpose, the application of cation-exchange chromatography or extraction chromatography with a resin coated by solution of (4,4′(5′)-di-t-butylcyclohexano-18-crown-6) in octanol-1 (Sr-resin, TrisKem International, France) is required [11,12]. However, the complete ion-exchange separation of strontium from other metals is not possible without high efficiency ion chromatographic separation after dilution of seawater samples (see discussion later in Introduction). Only 60% recovery of strontium was found for the use of extraction chromatography with Sr-resin [13].

Unsurprisingly, in many cases using the above instrumental methods, time consuming sample preparation or substantial dilution of seawater samples is recommended to improve analytical performance.

Ideally, accurate determination of mg L^{-1} concentration levels of strontium in seawater benefits from its separation from other alkaline earth metals, which are present at much higher concentration levels (the ratio of Sr^{2+}/Mg^{2+} is ~1/140 and Sr^{2+}/Ca^{2+} is ~1/65), and also from other major ionic components, most notably the ~0.52 mol L^{-1} concentration of NaCl. Ion chromatography (IC) has long been an obvious choice for this task [14]. However, ion-exchange separation of brines and seawater, which contain excessive amounts of alkali to alkaline-earth metals, using common ion-exchange resins, is subject to problems of serious overloading of ion-exchange sites, large chromatographic peaks of matrix ions masking peaks of minor components, and serious baseline disturbances. Additionally, the use of conductivity detection in traditional IC means analysis becomes nearly impossible without substantial sample dilution (approx. 130–500 times), which can lead to serious errors in final quantitation [15–19]. The alternative method is spectrophotometric detection. However, in this case post-column reaction with colour forming reagents is required [20].

Other analytical separation techniques, which have been reported for the determination of strontium in seawater, also have serious limitations, not least complexity and robustness, such as those reported combining capillary isotachophoresis (ITP) with cationic ion chromatography [21] or with capillary zone electrophoresis (CZE) [22]. Indeed, given the above complexity of the sample and analysis, remarkably to-date no chromatographic or electrophoretic methods for the direct (undiluted) determination of strontium in seawater have been reported.

In the last decade high-performance chelation ion chromatography (HPCIC) has received recognition as a simple and reliable method for the analysis of complex samples, including brines, seawater, and various industrial high ionic strength solutions [23]. The separation mechanism in HPCIC is based on the formation of labile complexes of metal ions with immobilised chelating ion-exchange groups, so the retention of metal ions (commonly alkaline earth and transition metal ions) is significantly less sensitive to the ionic strength of the samples, which translates to minimal sample pretreatment, and the possibility of the analysis of filtered undiluted seawater samples by direct injection onto the chromatographic column.

HPCIC has been used in the past for the separation and determination of strontium in saline samples, namely Antarctic lake samples [24]. The reported method used a Hamilton PRP-1 (150 × 4.1 mm I.D.) column packed with 5 micron neutral poly(styrene-divinylbenzene) (PS-DVB) spherical particles, which had been dynamically coated with the chelating ligand o-cresolphthalein complexone (o-CPC). However, prior to analysis the sample was diluted 1:15 with deionised water to minimise the effects of excessive amounts of Mg^{2+}. Also, to stabilise the column coating o-CPC was added to the mobile phase, complicating the system, which also required gradient elution to obtain the

separation, resulting in substantial disturbances of the baseline. Additionally, the separation efficiency of the coated column was unsatisfactory, resulting in poor peak shapes even under gradient elution conditions.

Recently, the chromatographic performance of columns, and typical peak efficiencies obtained using HPCIC have substantially improved. Monolithic columns have shown particular potential for use in HPCIC, most notably for fast HPCIC based methods, as a result of their lower operational backpressures and thus the possibility of operation at higher linear velocities whilst maintaining good peak efficiencies, as compared to particles packed beds [25]. To-date publications on the application of monolithic columns in HPCIC have utilised commercially available silica-based monoliths, additionally modified with iminodiacetic acid IDA or lysine functional groups [26–28].

The aim of the present work was to develop a fast, accurate and robust chromatographic method for the direct determination of strontium in undiluted seawater samples. The following paper describes a developed HPCIC method based upon the use of IDA bonded monolithic silica columns, which provide the efficiency and selectivity required for the separation and quantitation of the strontium peak. The effects of mobile phase composition and flow rate on the separation were investigated, as were various post-column reagents, which were compared to provide optimum responses to alkaline-earth metal cations, and particularly to deliver sensitive detection of strontium.

2. Experimental

2.1. Chemicals and reagents

The reagents used for column modification, namely 3-glycidoxy-propyltrimethoxysilane and iminodiacetic acid (IDA), were both purchased from Sigma-Aldrich (Gillingham, UK or Sydney, Australia). Methylthymol blue (MTB) or 3,3′-bis[N,N-di(carboxymethyl) aminomethyl]thymol-sulfonephthalein (99% dye content), and o-cresolphthalein complexone (o-CPC) or 3,3′-bis[N,N-di(carboxymethyl)-aminomethyl]-o-cresolphthalein (99% dye content), were obtained from Fluka (Buchs, Switzerland). Xylenol orange (XO) or 3,3′-bis [N,N-bis(carboxymethyl)-aminomethyl]-o-cresolsulfonephthalein tetrasodium salt (90% dye content), and 4-(2-pyridylazo) resorcinol (PAR) (96% dye content) were obtained from Sigma-Aldrich (Sydney, Australia). All chelating dyes were used without further purification.

Hydrochloric acid, nitric acid, acetic acid, ammonia, glycolic acid, sodium hydroxide, and sodium chloride were supplied by Sigma-Aldrich (Sydney, Australia). Boric acid and Spectrosol atomic absorption standard solutions of Ca^{2+}, Sr^{2+}, Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+} and Zn^{2+}, with concentrations of 1.00 g L^{-1} were purchased from BDH Chemicals (Poole, UK). An International Association for the Physical Sciences of the Oceans (IAPSO) normal standard seawater sample, batch P149 (5/10/2007), salinity 34.994 was supplied by OSIL (Havant, UK). Deionised water was supplied from a Milli-Q system (Millipore, Bedford, USA).

2.2. Instrumentation

For the chromatographic studies and sample analysis two chromatographic systems were used. The first was a Metrohm ion chromatography system, comprising model 844 compact IC with built in peristaltic reagent pump and post-column reactor, 830 IC interface (Metrohm, Herisau, Switzerland) and a Shimadzu UV/Vis detector, model SPD-10AV (Shimadzu, Kyoto, Japan). ICNet 2.3 SR4 software (Metrohm, Herisau, Switzerland) was used for data acquisition and processing of chromatograms. The second chromatographic system used was based upon a Waters 2695 separation module, a dual wavelength absorbance detector model 2487 (Waters, Milford, MA, USA), and an Eldex (Eldex Laboratories, Inc., Napa, CA, USA) PEEK-lined pump for delivery of the post-column reagents. Empower 3 software