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Short communication

Speciation analysis of inorganic tin by on-column complexation ion chromatography with inductively coupled plasma mass spectrometry and electrospray mass spectrometry

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ABSTRACT

Inductively coupled plasma-mass spectrometry (ICP-MS) and electrospray mass spectrometry (ESI-MS) were used as complementary methods to identify Sn-pentaacetic acid (DTPA) complex formation. ESI-MS was used to initially confirm the formation of $[Sn(DTPA)]^{3-}$ and $[Sn(DTPA)]^{1-}$ and their MS spectra suggest these tin complexes were stable in solution. On-column complexation of tin with DTPA and the separation of $[Sn(DTPA)]^{3-}$ and $[Sn(DTPA)]^{1-}$ was performed on anion-exchange chromatography with an mobile phase containing 20 mM NH_4NO_3 and 3 mM DTPA at pH 6.0, and the subsequent detection of $[Sn(DTPA)]^{3-}$ and $[Sn(DTPA)]^{1-}$ was achieved by ICP-MS. Linear plots were obtained in a concentration range of 1.0–1000 $\mu g\,L^{-1}$ with detection limits ranging from 0.1 to 0.3 $\mu g\,L^{-1}$. The developed procedure allows the simultaneous determination of $[Sn(DTPA)]^{3-}$ and $[Sn(DTPA)]^{1-}$ in less than 5 min with a RSD between 2.1 and 2.7%. The recoveries of $[Sn(DTPA)]^{3-}$ and $[Sn(DTPA)]^{1-}$ were found to be 96.8 and 99.4%, respectively, when the sample was spiked with 20 $\mu g\,L^{-1}$ standard. Finally, the proposed procedure was used for the determination of tin species in contaminated water.

1. Introduction

Tin and organotin compounds have been widely used for a variety of industrial and agricultural applications including tinplate products, pesticides, fungicides and anti-fouling agents [1,2]. Releases of tin into environmental media may occur from the production and use of tin and tin compounds, and have become a serious environmental threat [3,4]. Although inorganic tins (Sn(II) and Sn(IV)) are considered as less toxic as organotins, they cause increased toxicity to animals and human beings when inorganic tin compounds are transformed into their methylated forms [5]. Studies on the methylation of inorganic tin have attracted great interest because of their tendency to bioaccumulate through primary producers in aquatic ecosystems [6]. The toxicity and biological activity of tin relate to the state of oxidation of its inorganic forms [7]. Therefore, the risk assessment of tin pollution in the environment requires chemical speciation of the metal which influences the bioavailability and toxicity of the contaminants of interest [8].

Various approaches have been proposed for speciation analysis of Sn(II) and Sn(IV), with most of them are based on polarographic and voltammetric methods [9–13]. The main limitations of these electrochemical methods are the interfering effect from associated ions and the insufficient sensitivity and stability for analysis of the samples [7]. In order to determine trace or ultra-trace species in environmental samples, a convenient and reliable separation or preconcentration step is often necessary prior to element-selective or molecule-selective detection technique for speciation analyses [14,15]. For example, a procedure based on anion exchange resin separation and graphite furnace atomic absorption spectrometry (GFAAS) detection has been proposed for the determination of inorganic tin species [16]. The results shown that under the same condition, Sn(IV) was selectively adsorbed on the resin, but Sn(II) was not. Thus, a separation of Sn(II) and Sn(IV) was achieved [16]. More recently, a sophisticated method was reported for the determination of Sn(II) and Sn(IV) by inductively coupled plasma-optical emission spectrometry (ICP-OES) in combination with solid phase micro-extraction using barker yeast. Using this procedure, selective retention of Sn(IV) by yeast at pH 2.0 and Sn(II) in solution were realized and the determination of tin in the solid phase was easily carried out by submitting slurry of yeast directly to ICP-OES [7]. These methods are generally useful for the analysis of tin species.

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It has become a common practice in recent years to use inductively coupled plasma-mass spectrometry (ICP-MS) for ultra-sensitive detection of trace element of interest [17]. However, ICP is a destructive ionization source. Conventional ICP-MS serves as an ultra-sensitive elemental detector only, and it is unable to provide inherent information about chemical species [18]. Thus, a separation step is a prerequisite for speciation analysis prior to the determination of elemental composition in the given chemical species by ICP-MS. In addition, for speciation analysis of known chemical species, standards are needed for compound identification via matching with retention times during separation processes, but standards are not always available [18]. For speciation analysis of unknown chemical species or where chemical standards not available, one of the most commonly applied techniques for compound identification is electrospray ionization-mass spectrometry (ESI-MS) [15]. The 'soft' ionization of ESI produces intact molecular ions without any significant fragmentation and a series of multiply charged peaks for many heavy compounds, permitting a very accurate determination of molecular weights [18]. ICP-MS and ESI-MS, coupled to a separation technique have already been applied by a large number of researchers as complementary methods, providing elemental and molecular information that together provide a complete picture of elemental speciation [15,18–20]. To our best knowledge, there is no report on the analysis of Sn (II) and Sn (IV) by ion-exchange chromatography (IC) ICP-MS and confirmation of them by ESI-MS. For these reasons, the present study was to develop tin speciation analysis based on separation of Sn-DTPA complexes formed on column by IC, molecular identification by ESI-MS and detection of the species by ICP-MS. The proposed method was used for speciation analysis of inorganic tin species in contaminated waters.

2. Experimental

2.1. Chemicals and solutions

All chemicals used in this study were of analytical reagent grade from Sigma and Aldrich (Sydney, Australia). Ultra pure water with a specific resistance of 18.2 MΩ cm^{-1} (Milli-Q Plus system, Millipore, Bedford, MA, USA) was used for preparing all solutions and standards. Standard solutions of $SnCl_2{\cdot}2H_2O$ and $SnCl_4{\cdot}5H_2O$ were prepared daily from a 1 mM stock solution in 0.1% (v/v) HNO_3 solution and diluted to the required concentrations before use. Eluents required for IC-ICP-MS were prepared by dissolving an appropriate amount of ammonium salts and DTPA in MilliQ^{TM} water, filtered through a 0.45 μm cellulose acetate membrane filter and degassed in an ultrasonic bath. The eluent was adjusted to pH 6.0 with 0.1 M ammonium hydroxide and nitric acid. Water collected from contaminated site (Mawson Lake, South Australia) was also filtered through a 0.45 μm cellulose acetate membrane filter prior to speciation analysis in duplicate.

2.2. ESI-MS system and IC-ICP-MS conditions

Flow injection analysis was carried out using an Agilent 1100 series instrument equipped with an injector (Agilent, Waldbornn, Germany). The carrier solution contained 5 mM ammonium acetate (NH_4Ac, pH at 6.0) at flow-rate of 0.5 mL min^{-1}, with a 10 μL injection volume of samples. The complexation of Sn (II) and Sn (IV) with DTPA was achieved by mixing aqueous solutions of Sn (II) and Sn (IV) with DTPA at a 1:1 mole ratio in 15 mL polypropylene tubes, respectively, and the mixed solutions stand at room temperature for 24 h prior to use. The MS system was an Agilent 1100 series quadrupole equipped with electrospray ionization (ESI) source and was operated in the negative ionization mode. The operating conditions for ESI were: nebulizer nitrogen gas at 40 psi; drying nitrogen gas flow rate at 12 L min^{-1}; capillary voltage at −4000 V and gas temperature of 350 °C. The fragmentor voltage was maintained at 90 V.

An Agilent 1100 liquid chromatography module (Agilent, Tokyo, Japan) with a 4.6 mm × 150 mm separation column (G3154A/101) with a stationary phase based on a porous polymethacrylate resin (10 μm particle size and exchange capacity of 50 μeq g^{-1}) equipped with a 4.6 mm × 10 mm guard column (G3154A/102) were used. The samples were injected using an 1100 auto-sampler using an injection volume of 50 μL, with a flow-rate of 1.0 mL min^{-1}. The outlet of the separation column was directly connected to a Babington nebulizer of an Agilent 7500c ICP-MS (Agilent, Tokyo, Japan), which served as an element-specific mass detector. Tin was detected at m/z 118 and 120. The ICP-MS conditions were as follows; RF power: 1450 W; plasma argon gas flow: 15 mL min^{-1}; auxiliary argon gas flow: 1.0 mL min^{-1}; carrier argon gas flow: 1.20 mL min^{-1}; sampling depth: 7.5 mm; integration time: 1 s; dwell time: 0.5 s. The IC-ICP-MS system was controlled and the data was processed using the Agilent Chemstation software package.

3. Results and discussion

3.1. Confirmation of the formation of Sn-DTPA complexes

The confirmation of formation of Sn-DTPA complex by ESI-MS is necessary because the ligand exchange between metal complex and anion in the buffer is often observed during the separation of metal complexes [21]. Under optimized ESI source conditions, it has been shown that Sn-DTPA complex in solution can be reflected in the gas phase [19,22]. The ESI-MS spectra for Sn-DTPA complexes were determined in the negative ion ESI mode with a carrier solution containing 5 mM NH_4Ac at pH 6.0 under the optimized conditions for ionization (fragmentor voltage 90 V and capillary voltage −4000 V) due to these parameters significantly affecting the fragmentation within the source. Fig. 1a shows the ESI-MS spectrum of DTPA where the dominant gas phase ions were in the form of $[M{-}H]^-$, where M represents DTPA, corresponding to $[\text{DTPA-H}]^-$ at m/z 392.3. In addition, another peak, corresponding to the gas phase ions $[\text{DTPA-2H}^+\text{Na}]^-$ was also observed at m/z 414.3. To understand the complexation of Sn (II) and Sn(IV) with DTPA, a 5 mg L^{-1} mixtures of Sn (II), Sn(IV) and DTPA (mole ratio = 1:1) were injected into the ESI-MS system. The MS spectrum in Fig. 1b shows prominent ions at m/z 505.5 and 507.5, corresponding to $[\text{DTPA-3H+Sn}]^-$ and $[\text{DTPA-5H+Sn}]^-$, respectively. This identifies the 1:1 stoichiometry of $[\text{Sn(DTPA)}]^{3-}$ and $[\text{Sn(DTPA)}]^-$, and the complexes were formed and stable in the solution. Furthermore, the ESI-MS detection of these tin complexes is specific since tin has been selected three stable isotopes [^{116}Sn(14.54%), ^{118}Sn(24.22%), ^{120}Sn(32.58%)] and consequently the Sn complexes have a very distinctive isotope pattern. For example, as shown in Fig. 1b, $[\text{DTPA-3H+Sn}]^-$ for Sn(II) has three complex isotope peaks corresponding to the selected three Sn isotopes at m/z 505.5, 507.5, 509.5 and $[\text{DTPA-5H+Sn}]^-$ for Sn (IV) also have three selected isotopes at m/z 503.5, 5055 and 507.5. The peaks at m/z 505.5 and 507.5 are much higher than the other peaks, which is a result of overlaps of $[\text{Sn(DTPA)}]^{3-}$ and $[\text{Sn(DTPA)}]^{1-}$. The results indicated that $[\text{Sn(DTPA)}]^{3-}$ and $[\text{Sn(DTPA)}]^{1-}$ were present in aqueous solution, and therefore should be possible to use IC-ICP-MS for detection and speciation.

3.2. On-column complexation and separation

On-column complexation enables the formation of a stable metal complex that is suitable for chromatographic separation [23].