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Analytical Methods

Use of an aminated Amberlite XAD-4 column coupled to flow injection cold vapour generation atomic absorption spectrometry for mercury speciation in water and fish tissue samples

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ABSTRACT

An aminated Amberlite XAD-resin as a solid phase extractant was tested for speciation of inorganic mercury, Hg(II) and methylmercury, MeHg(I) in water and fish tissue samples. It was found that Hg(II) and MeHg(I) ions could be simultaneously retained by a column filled with AAXAD-4 resin at pH 4 and the sequential quantitative elutions of Hg(II) and MeHg(I) were achieved using 10 mL of 0.1%(m/v) thiourea in 3%(v/v) HCl and 10 mL of 6 mol L^{-1} HCl, respectively. Hg(II) in the eluent was directly determined and MeHg(I) in the second eluent is quantified using FI-CVG-AAS after its oxidative digestion with $KMnO_4$. The limits of detection for Hg(II) and MeHg(I) ions were found to be 0.148 and 0.157 µg L^{-1}, respectively. The method was validated by analysing a certified reference material. The relative errors for Hg(II), MeHg(I) and *T*-Hg were in range of −1.8% and −3.2%.

1. Introduction

Mercury (Hg) is known as one of the most hazardous heavy metals impacting on human health and ecosystem because of its high toxicity and accumulative properties (Tuzen, Karaman, Citak, & Soylak, 2009). The toxicity, bioavailability and mobility of mercury depend on not only its total concentration, but also strongly its chemical form (Yun, He, Wang, Wang, & Jiang, 2013). Although, all forms of mercury are toxic, methyl mercury is the most poisonous due to its high bioaccumulation capacity through the aquatic food chain (Bosch, O'Neill, Sigge, Kerwath, & Hoffman, 2016; Leopold, Foulkes, & Worsfold, 2009). In complicated matrices such as environmental, biological and food samples, mercury species are found to be at ultra-trace levels. In natural waters, while total mercury levels change between 0.2 and 100 ng L^{-1}, methylmercury levels are usually found to be much lower in the order of 0.05 ng L^{-1} (Cossa, Sanjuan, Cloud, Stockwell, & Corns, 1995; Horvat, Liang, & Bloom, 1993). The World Health Organization (WHO) permits a limit of 1 ng mL^{-1} Hg in drinking water (Balarama Krishna, Chandrasekaran, & Karunasagar, 2010). The maximum permitable methylmercury, MeHg(I) concentration for the consumption of fish and shellfish recommended is 300 µg kg^{-1} of wet mass of fish tissue by the US EPA (United States Environmental Protection Agency, 2006). The same limit for total mercury in fish is set by the European Union as 500 µg kg^{-1} of wet mass of fish tissue (Directive, 2005). It is known that mercury alone causes various neurologic diseases like Alzheimer's disease, Parkinson's disease and Huntington's disease (Mutter, Naumann, Sadaghiani, Walach, & Drasch, 2004) and also it causes damage on the immune system and kidneys (Wang, Feng, Anderson, Xing, & Shang, 2012). Additionally, in the form of methylmercury, it causes brain (Minamata disease), cardiovascular and nervous system damages (Wang, et al., 2012). Therefore, the Agency for Toxic Substances and Disease Registry (ATSDR) evaluates mercury as one of the priority hazardous substances.

Based on the above reasons, the development of reliable analytical methods for the speciation analysis of mercury in waters and sea foods is of significant importance to protect the environment and provide food safety. Sensitive element-specific detection techniques such as cold vapour atomic absorption spectrometry (CV-AAS) (Almeida, Oliveira, Silva, & Coelho, 2016; Shah, Kazi, Baig, Afridi, & Arain, 2012), cold vapour atomic fluorescence spectrometry (CV-AFS) (Yun et al., 2013), graphite furnace atomic absorption spectrometry (GF-AAS) (Moraes et al., 2013), inductively coupled plasma atomic emission spectrometry

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(ICP-AES) (Wuilloud, Wuilloud, Silva, Olsina, & Martinez, 2002), inductively coupled plasma-mass spectrometry (ICP-MS) (Balarama Krishna, et al., 2010; Batista, Rodrigues, de Souza, Souza, & Barbosa, 2011) for mercury determination are currently available. Despite several instrumental advantages, these detection techniques do not have adequate sensitivity and selectivity for the speciation of mercury species at ultra-trace or trace level in environmental and biological samples having complicated matrices. For this reason, the selective preconcentration of mercury species prior to their measurements is essential. Solid phase extraction (SPE) is one of the most adequated methods for preconcentration of trace element species among the various preconcentration techniques (Lemos, & dos Santos, 2014; Behbahani et al., 2013). Depending on the nature of the sorbent, the selectivity is provided with the retention of species at different pHs, selecting suitable chelating ligand and selective eluent. Until now, various solid phase materials such as polyaniline (Balarama Krishna, et al., 2010), Fe_3O_4 magnetic nanoparticles functionalized with dithizone(Adlnasab, et al., 2014), Amberlyst 36 (Turker, Çabuk, & Yalçınkaya, 2013), Dowex Optipore SD-2 immobilized with streptococcus pyogens (Tuzen, Uluozlu, Karaman, & Soylak, 2009), Amberlite XAD-4 functionalized with BTAC (Lemos, & dos Santos, 2014) have been used for mercury speciation. Among these solid phases, due to its excellent stability in wide pH range, readily availability and easy derivatization, Amberlite XAD-series resins continue to be the most attractive solid phase materials. Recently, Amberlite XAD-4 modified by introducing amino groups into the aromatic ring has been reported for the removal of fluoride and chromium (VI) ions from aqueous solutions by batch technique (Bhatti, Memon, Memon, Ali Bhatti, & Solangi, 2017; Solangi, Memon, & Bhanger, 2009). Additionally, we have applied it successfully for chromium speciation by using a column technique (Aksoy, Elci, Siyal, & Elci, 2018). However, based on literature search no such study has been reported to date on the use of aminated Amberlite XAD-4 (AAXAD-4) resin for mercury speciation and preconcentration of mercury species. In solid phase extraction studies, AAXAD-4 promises a significant future because of its high affinity to metal ions and ion exchange capacity depending on pH of sample solution (Bhatti et al., 2017; Solangi et al., 2009). Additionally, in previous researches, polyaniline (PANI) having amino groups was used as SPE sorbent which showed a high affinity for Hg(II) and MeHg(I) species (Balarama Krishna, Karunasagar, Rao, & Arunachalam, 2005; Gupta, Singh, & R.A., & Dubey, S.S., 2004). In the basis of these researches and the structural similarities present between PANI and the AAXAD-4, our expectation was the adsorption of mercury species on AAXAD-4.

Based on the reasons above, in this study, the speciation of mercury species has been performed using AAXAD-4 resin to retain Hg(II) and MeHg(I) and then sequential elutions of both species was done and their determination in the effluent was carried out with Flow injection-cold vapour generation-atomic absorption spectrometric (FI-CVG-AAS).

2. Materials and methods

2.1. Instrumentation

Flow injection-cold vapour generation-atomic absorption spectromeric (FI-CVG-AAS) measurements were carried out by using a Perkin Elmer AAS 700 atomic absorption spectrometer equipped with a Perkin Elmer FIAS-100 Flow Injection System and an electrically heated quartz tube atomizer (QTA) for determinations of Hg(II) and after oxidative digestion of MeHg(I). A mercury EDL (Perkin-Elmer) operated at 185 mA was used as the radiation source. The wavelength and slit were set to 253.7 and 0.7 nm, respectively. The instrumental parameters optimized experimentally for cold vapour generation: atomizer temperature 120 °C, injection volume 500 µL, carrier solution 4% (v/v) HCl, reducing agent 0.2% (w/v) $NaBH_4$ in 0.05% (w/v) NaOH.

Digital pH meter connected with a combined glass calomel electrode (a WTW 720 model pH meter, Weilheim, Germany) was used for pH measurements of aqueous solutions.

Polyvinyl chloride (PVC) column with stopcock and the frits (porosity 20 µm) was used for preconcentration experiments. The solutions were passed through the column by a vacuum manifold (J.T Baker brand with 12 ports from Germany).

ATR-IR spectrometer (UATR two model from PerkinElmer) was used for recording ATR spectra.

2.2. Chemicals and reagents

All chemical reagents used were analytical grade. Aqueous solutions were prepared with Ultra-Pure (UP) quality water (resistivity 18.2 MΩ cm^{-1}) obtained from reverse osmosis system (Human Corp. Seoul, Korea). Working solutions of Hg(II) were prepared daily in UP water by appropriate dilution of a 1000 mg L^{-1} Hg(II) stock standard solution purchased from Merck (Darmstadt, Germany). The stock solution of MeHg(I) (1000 mg L^{-1}) was prepared in methanol (Sigma-Aldrich, Steinheim, Germany) by dissolving the MeHgCl salt having a purity of 99.9% obtained from Fluka (Steinheim, Germany). Every day the working solution of MeHg(I) to be used throughout this work was prepared freshly.

The $NaBH_4$ (Merck) solutions in the range of 0.05–0.5% (m/v) were prepared freshly in 0.05% (m/v) NaOH. Solutions of NaOH in the range of 0.025–0.125% (m/v) including 0.2% (w/v) $NaBH_4$ were prepared freshly by dissolving solid NaOH (Merck) in UP water. Solutions of HCl in the range of 1.0–5.0% (v/v) were obtained by appropriate dilution of concentrated HCl of 36.5–38.0% (Merck). An oxidizing solution was prepared by dissolving $KMnO_4$ (Merck).

The required solutions of diverse ions were prepared by dissolving their appropriate salts. Thiourea solutions at different concentrations were prepared by dissolving the required amount of thiourea obtained from Merck in the range of 0.5–3% (v/v) HCl.

Buffer solutions used for adjusting pH of the solutions were as follows: potassium chloride-hydrochloric acid for pH 2.0, acetic acid-sodium acetate for pH 3.0–6.0, sodium dihydrogen phosphate-sodium monohydrogen phosphate for pH 7.0 and ammonia-ammonium chloride for pH 8.0–9.0.

The standard reference material (SRM), NRCC-DORM 4 Dogfish Muscle, used to verify the procedure was supplied from National Research Council of Canada (Ottawa).

2.3. Synthesis

AAXAD-4 resin was synthesized from commercial Amberlite XAD-4 resin (Fluka, Germany) by using previously reported method (Solangi et al., 2009). The synthesized resin was confirmed by comparing FT-ATR spectra of Amberlite XAD-4 (Fig. S1a), Amberlite XAD-4-NO_2 (Fig. S1b) and Amberlite XAD-4-NH_2 (Fig. S1c). The formation of AAXAD-4 is identified with aromatic ammine peaks at 3359 cm^{-1} and 3217 cm^{-1} for $-NH_2$ streching vibrations.

2.4. Sampling

We collected the water samples having different matrices, such as hot spring water (it is known as red water, because of high levels of iron oxide, Karahayıt district of Denizli-Turkey, Aegean sea surface water from Güvercinlik bay (Bodrum-Turkey) and waste water from inlet and outlet of the wastewater treatment plant in Denizli-Turkey. The water samples were filtered through 0.45 µm cellulose nitrate membrane (Sartorius, GmbH, Germany) under vacuum to remove possible suspended matters and then immediately analysed by the purposed procedure.

The seafood samples: *levrek* (perch, Dicentrarchus labrax from Aegean sea, Didim-Turkey), *istavrit* (horse mackerel, trachurus mediterraneus from Mediterranean sea, Antalya-Turkey), *gopez* (boops boops