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Ultra-trace analysis of silver and platinum in seawater by ICP-SFMS after off-line matrix separation and pre-concentration

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ABSTRACT

Precise and accurate quantification of Ag and platinum group elements in marine, estuarine and riverine waters is challenging due to the complex matrices and ultra-low concentrations in the pmol kg^{-1} and fmol kg^{-1} range. A methodological approach has been developed for the analysis of Ag and Pt in seawater based on the extraction of their anionic chloro-complexes utilizing the strong anion exchange resin Dowex™ 1-× 8 in an off-line matrix separation and pre-concentration approach prior to determination by ICP-SFMS. The method allows simultaneous processing of four 100 mL samples at a flow rate of up to 2 mL min^{-1} in an ultra-clean manifold. Enrichment factors of 40 could be achieved with elution into 2.5 g of a mixture of HNO_3/HCl, yielding adequately low detection limits to obtain open ocean profiles. Quantification was performed by matrix-matched calibration and internal standardization. To validate the accuracy of this approach, isotope dilution analysis was also used. The applicability of the method was demonstrated on a suite of reference samples and depth profiles collected during the 2009 2nd U.S. GEOTRACES Intercalibration cruise in the eastern North Pacific.

1. Introduction

Although Ag and other precious metals are not key trace elements included in programs in chemical oceanography such as GEOTRACES (GEOTRACES Science Plan, 2006), there is increasing interest about their concentrations and distributions in oceanic, coastal, estuarine and riverine waters. Ag is known as highly toxic to marine invertebrates, phytoplankton and seaweed due to bioaccumulation (Ratte, 1999) but little is known about the environmental effects or fates of platinum group elements (PGEs) which are now increasingly used in various industrial catalysts, automotive catalysts and anti-cancer medical applications (Gonzáles García et al., 2003). Furthermore, Ag, and PGEs can be used as geochemical tracers (Gallon and Flegal, 2015; Rauch and Morrison, 2008) for biogeochemical cycling in oceanic waters. However, accurate quantification of these metals in seawater is challenging due to the extremely low concentrations and the saline matrix, hence, direct analysis is difficult.

Atomic spectroscopic and spectrometric techniques published for the analysis of Ag include graphite furnace/electro thermal atomic absorption spectrometry (GF-AAS/ET-AAS) (Martin et al., 1983; Sanudo-Wilhelmy and Flegal, 1992; Smith and Flegal, 1993; Benoit et al., 1995; Miller and Bruland, 1995), laser-excited atomic fluorescence spectrometry (Gornushkin et al., 1996) and (isotope dilution)-inductively coupled plasma (sector field) mass spectrometry ((ID)-ICP-(SF)MS) (Falk et al., 1997; Yang and Sturgeon, 2002; Barriada et al., 2003; Turetta et al., 2004; Ndung'u et al., 2006; Valverde et al., 2008). Traditionally for Ag assays, liquid-liquid extraction using ammonium 1-pyrrolidinedithio-carbamate/diethylammonium diethyldithiocarbamate (APDC/DDDC) as described by Bruland and Franks (1979) for the pre-concentration of Cu, Cd, Zn and Ni has been applied (Martin et al., 1983; Smith and Flegal, 1993). In addition, co-precipitation- and flotation techniques were developed (Bloom and Crecelius, 1984; Čnudeva and Statilov, 1997). However, these techniques are time consuming, utilize hazardous reagents and require large sample and reagent volumes. Direct determination of Ag amongst other metals was reported using ET-AAS with chemical modifiers (Bermejo-Barrera et al., 1998), ICP-MS (Falk et al., 1997) or ICP-SFMS and PFA micro flow nebulization/desolvation for solvent evaporation (Turetta et al., 2004). Due to the limited matrix tolerance of the ICP-MS interface, direct analysis of seawater samples requires dilution of the sample and/or a careful optimization of operating conditions to overcome matrix effects. However, this dilution also increases the detection limits and severely limits the method's usefulness for oceanic waters at picomolar and femtomolar concentrations. In recent years, solid phase extraction (SPE) procedures were published using silica-immobilized 8-hydroxyquinoline (Benoit et al., 1995), chelating ion exchange resins (Valverde et al.,

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2008) (Chelex-100; styrene divinylbenzene copolymers containing paired iminodiacetate ions) and strong anion exchangers (AG 1-X; styrene-divinylbenzene immobilized trimethylbenzylammonium functional groups), respectively, as sorption materials either in batch or continuous extraction mode. The latter was used by various researchers in an online mode directly coupled to the ICP-MS (Yang and Sturgeon, 2002; Barriada et al., 2003; Ndung'u et al., 2006).

SPE on the anion exchange resin AG 1-× 8 has also been used for the enrichment of Pt prior to ET-AAS (Gonzáles García et al., 2003) and ID-ICP-MS analysis (Colodner et al., 1993; Suzuki et al., 2014), respectively.

Besides atomic spectroscopic and spectrometric techniques, voltammetry techniques have also been developed for the determination of Pt in water samples at ultra-trace concentrations (Van den Berg and Jacinto, 1988; Cobelo-García et al., 2014).

In the present work, we report the development and optimization of a method for the accurate quantification of Ag and Pt in seawater, which may be used on a large scale for quantification of these metals in samples collected on future GEOTRACES cruises and other environmental monitoring programs. At typical seawater conditions (3.5% salinity, pH > 7), dissolved Ag and Pt are mainly present as inorganic chloride complexes; $AgCl_2^-$ and $AgCl_3^{2-}$ (Miller and Bruland, 1995) and $PtCl_4^{2-}$ and $PtCl_5(OH)^{2-}$ (Mashio et al., 2017). As a result, we investigated the use of an anion exchange resin to concentrate the anionic complexes from acidified (0.024 M HCl) seawater. The method is based on the extraction setup described by Biller and Bruland (2012) and uses standard addition and isotope dilution analysis (IDA) for the quantification of the elements of interest.

For validation, it has been applied to SAFe and GEOTRACES reference samples as well as samples from depth profiles from the 2009 2nd U.S. GEOTRACES intercalibration cruise.

2. Experimental section

2.1. Chemicals and laboratory materials

Ultra-pure water and mineral acids used for all samples and standards were prepared by single distillation with quartz dual-finger sub-boiling distillation units. Ultra-pure water (Q-H_2O) was prepared by sub-boiling distillation of (~18 MΩ cm^{-1}) Milli-Q® water (MQ-H_2O; Millipore Corp.) directly into a fluorinated high density polyethylene (HDPE) carboy (Nalgene®) for storage. Concentrated (65%, 15.8 mol L^{-1}) Trace Metal™ grade nitric acid (TMG-HNO_3; Fisher Scientific) was sub-boiling distilled to produce 15.8 mol L^{-1} Q-HNO_3 directly into, and stored in, fluorinated ethylene propylene (FEP) Teflon™ bottles until use. Due to a hydrochloric acid/water azeotrope, concentrated (37%, 12 mol L^{-1}) Trace Metal™ grade hydrochloric acid (TMG-HCl; Fisher Scientific) was diluted 1:2 by volume with MQ-H_2O to 6 mol L^{-1} prior to distillation to produce a more consistent final concentration of ~6 mol L^{-1} Q-HCl which is also an easier working solution with fewer corrosive fumes.

Certified 1000 mg L^{-1} single element standards for trace analysis (Ag, Hf, Hg, In, Lu) and a certified multi-element standard (ICP-MS 3) containing 10 mg L^{-1} each of Sb, Au, Hf, Ir, Pd, Pt, Rh, Ru, Te and Sn were purchased from SPEX (Metuchen, NJ). A standard solution enriched in ^{109}Ag (abundance = 99.41%, 99.93 ± 1.69 μg g^{-1}) was purchased from ISC Science, Oviedo, Spain. Isotopically enriched ^{196}Pt (abundance = 97.25%) was obtained from the Science Technical Centre "Stable Isotopes" of State Scientific Centre of the Russian Federation – Institute of Physics and Power Engineering, Obninsk, Kaluga Region, Russia and prepared and quantified by applying reverse isotope dilution mass spectrometry (IDMS) as described in Kanitsar et al. (2003).

Dowex™ 1-× 8 strong anion exchange resin in chloride form (100–200 mesh and 200–400 mesh) was purchased from Supelco (Bellefonte, PA). Open ocean surface seawater used for seawater standard additions was collected using trace metal clean sampling techniques, either far offshore coastal California during a cruise in August 2011 (CUTZ II) or in the South Pacific gyre during the 2013 GEOTRACES GP16 cruise, filtered with 0.2 μm PCTE cartridge filters (Osmonics™) and acidified with 4 mL L^{-1} of 6 mol L^{-1} Q-HCl (0.024 mol Q-HCl L^{-1}, pH ~1.8). The acidified seawater (0.024 mol Q-HCl L^{-1}) used for standard additions was pre-cleaned to remove the targeted elements by pumping through a Poly-Prep® Chromatography column, 12 mL total volume, (Bio-Rad Lab, Hercules, Ca) filled with Dowex™ 1-× 8 resin (100–200 mesh) at a flow rate of approximately 2 mL min^{-1}.

For quality control the following reference samples, collected during the SAFe (Sampling and Analysis of Fe) program and the GEOTRACES Intercalibration North Atlantic and North Pacific cruises by Ken Bruland and Geoffrey Smith, were assayed: SAFe North Pacific open ocean surface and deep water (SAFe S surface and SAFe D2 1000 m), GEOTRACES Surface Pacific (GSP, SAFe site) and GEOTRACES Surface Coastal (GSC; Santa Barbara Basin coastal site). These samples were all acidified to 0.024 mol Q-HCl L^{-1} (pH ~1.8) and stored in LDPE bottles.

An ultraviolet irradiation apparatus consisting of a low-pressure mercury vapor grid lamp was used for UV treatment of seawater samples (UVO-cleaner model 342, Jelight Inc., Irvine, CA). The UV intensity (approx. 16 mW cm^{-2}) was monitored daily using a digital radiometer (Model JX11, Jelight Inc., Irvine, CA). During UV treatment, the samples were contained in 120 mL Savillex perfluoroalkoxy (PFA) Teflon™ jars with quartz windows imbedded in modified lids and then transferred to the LDPE bottles used for the pressurized extraction manifold described below.

All LDPE bottles used for seawater samples, standards and elution reagents were cleaned following the same procedure as used for the SAFe and GEOTRACES Intercalibration sample bottles (see: http://www.geotraces.org/images/stories/documents/intercalibration/Cookbook.pdf). The 8 mL LDPE bottles (Nalgene®) used for storing elution extracts were soaked overnight in ~60 °C 3 mol L^{-1} reagent grade HCl (RG-HCl, Fisher Scientific), rinsed with MQ-H_2O, then soaked overnight in ~60 °C combined 4 mol L^{-1} TMG-HNO_3 and 0.5 mol L^{-1} TMG-HCl before final rinses with Q-H_2O and then dried on a Class-100 work bench.

The PFA Teflon™ jars and lids modified with quartz windows used for UV-irradiation treatment were rigorously acid cleaned by soaking one week each in ~60 °C 6 mol L^{-1} TMG-HCl and ~60 °C concentrated 15.8 mol L^{-1} TMG-HNO_3, one week at room temperature in TMG-aqua regia and then rinsed and filled with MQ-H_2O until residual acid dissipated. The PFA jars were conditioned with pH 2 seawater and tested until blanks were low and consistent. Between samples, the manifold extraction LDPE bottles and UV-irradiation PFA jars were briefly soaked in 1.5 mol L^{-1} TMG-HNO_3 and then rinsed with MQ-H_2O and new sample. Polystyrene (PS) 2 mL sample vials, polypropylene pipette tips and other equipment involved in the sample preparation and measurement processes were acid leached with 1 mol L^{-1} TMG-HNO_3, rinsed with MQ-H_2O and dried in a Class-100 clean bench before use. All sample weighing and preparation of reagents and standards were performed in a Class-1000 clean lab on metal free work benches. Sample seawater extractions were conducted in a Class-100-1000 metal free clean bench in a Class ≤ 10000 lab. ICP-SFMS measurements were carried out at the Institute of Marine Science at UCSC.

2.2. Extraction manifold and procedure

The pressurized off-line extraction manifold shown in Fig. 1A allowed processing of four samples simultaneously at flow rates up to approximately 2 mL min^{-1} with only LDPE or Teflon™ contacting the sample, rinse solution and elution acid before the resin columns. Four channels of an 8-channel peristaltic pump (Dynamax, Ranin) were