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Inorganic speciation analysis of selenium by ion chromatography-inductively coupled plasma-mass spectrometry and its application to effluents from a petroleum refinery☆

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Abstract

A new method for the speciation analysis of selenite (Se-IV), selenate (Se-VI), and selenocyanate ($SeCN^-$) is described and first results are presented on the distribution of these species in wastewater samples from a Brazilian oil refinery plant. The method is based on the ion chromatographic separation of these species followed by on-line detection of ^{77}Se, ^{78}Se, and ^{82}Se using quadrupole inductively coupled plasma-mass spectrometry (ICPMS). The system employed consisted of a HPLC pump equipped with a manual syringe loading injector, and an anion exchange column (Metrosep A Supp1), the latter interfaced with the ICPMS via a concentric nebulizer–cyclonic spray chamber sample introduction device. Several eluents already described in the literature for the speciation analysis of inorganic selenium were tested, permitting in most cases a good separation of Se(IV) and Se(VI), however, resulting all in very long residence times (>30 min) and associated peak broadening for the $SeCN^-$ ion. This drawback could be effectively avoided by using as the mobile phase a solution of cyanuric acid (3 mmol L^{-1}), modified with acetonitrile (2% v/v) and percchlorate acid (2.5 mmol L^{-1}). Typical retention times (s) for the three analyte species were: selenite (210) < selenate (250) < selenocyanate (450). Repeatabilities in peak position were better than 1% and in peak area evaluation about 3%. Absolute limits of detection (in ng) for these species using an ELAN 5000 instrument and a 500-μL sample injection loop are 0.04, 0.05 and 0.09, respectively. No certified reference materials were available for this study, however, results on spiked wastewater samples showed acceptable recoveries (80–110%) and repeatabilities (RSD <5%), thus validating this method for its intended purpose. Once optimized, the method was applied to wastewater samples from an oil refinery plant. In all samples until now analyzed, selenocyanate was by far the most abundant selenium species reaching concentrations of up to 90 μg L^{-1}. Selenite was detected only in one sample and selenate could not identified in any of the samples analyzed. Total concentrations of selenium in most samples, assessed by hydride generation ICPMS and by solution nebulization inductively coupled plasma optical emission spectrometry (ICPOES), exceeded those obtained from speciation analysis, indicating the presence of other selenium species not observed by the here used methodology.

Keywords: ICPMS; Ion chromatography; Selenium; Speciation analysis; Refinery wastewaters

1. Introduction

Due to its important role in life processes, selenium is one of the most studied elements as regard to biologically relevant species, and methods for their determination (e.g.,

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[1–4]). Contrarily, little information is available on the speciation of this element in industrial effluents. This issue has become important more recently when the first results were published on high concentrations of selenium in wastewaters, especially from refineries in which crude oils from seleniferous marine shale are processed [5–10]. Although being an essential element, the total maximum permissible concentration (MPC) for discharged wastewater is low, 0.050 mg L^{-1} and 0.020 mg L^{-1}, according to the Conselho Nacional do Meio Ambiente (CONAMA), Brazil [11], and the Companhia de Tecnologia e Saneamento Ambiental (CETESB-SP) [12], respectively. Surprisingly, these concentrations are lower than that for the generally considered more toxic arsenic (500 mg L^{-1} [11]).

Removal of selenium (and other elements) from wastewater is frequently performed by co-precipitation/coagulation procedures, whose efficiencies depend on the physico-chemical nature of the species present. Difficulties in removing selenium from oil refinery wastewaters have been reported by several authors and attributed to a selenocyanate species ($SeCN^{-}$) not co-precipitated by the conventional ferric salt process (e.g., [5,6]). In order to develop more efficient treatment processes, it is mandatory to have sensitive and robust methods, which can handle the very complex matrix of refinery wastewaters for the speciation analysis of selenite (Se-IV), selenate (Se-VI), selenocyanate ($SeCN^{-}$), and of other possible species, including organic ones. Up to now, ion chromatography (IC) coupled to inductively coupled plasma mass spectrometry (ICPMS) or to atomic fluorescence spectrometry (AFS) are the only promising techniques investigated for the required concentration range [13–15]. Concerning the speciation analysis of the two most prominent inorganic Se-species, selenite and selenate, a considerable number of methods have been published based on ion chromatography and differing in the column material, the mobile phase and the elemental detector used (e.g., review paper of Guerin et al. [1]). As a general feature, they permit the separation of selenite and selenate in short times (Se-IV: 2–4 min; Se-VI: 5–9 min) and with good detection limits (0.02–2 ng). However, none of those methods deals with the very complex matrix of refinery wastewater and includes the detection of the selenocyanate species. The presence of selenocyanate in wastewater from crude oil refineries was first mentioned by Lukasiewiz [16] in 1994, and the only speciation analysis methods we found in literature go back to Wallschläger and collaborators [14,15].

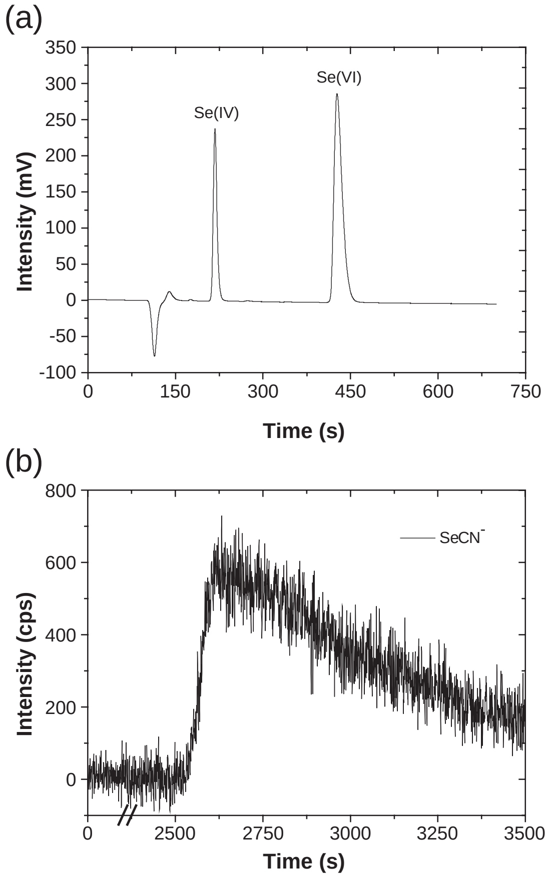

Fig. 1. Chromatograms showing the strong retention of selenocyanate as opposed to Se(IV) and Se(VI), amount of each species 100 ng, elution with: (a) 6 mmol L^{-1} sodium carbonate solution, suppressed ion conductivity detection; (b) with 50 mmol L^{-1} of the same eluent and ICPMS detection. For other experimental conditions, see Tables 1 and 2.

Different from Se(IV) and Se(VI), selenocyanate has a more complex chromatographic behavior, which is similar to that of other hydrophobic, large and polarizable anions, such as iodide, thiosulfate, and thiocyanate. These ions show strong interactions with most of the stationary phases used in ion chromatography, resulting in long residence times and consequent peak broadening (see Fig. 1b). Wallschläger and coworkers [14,15] could achieve much lower retention times for $SeCN^{-}$ (about 11 min) by the use of NaOH in a step gradient elution. To reduce the undesired high salt load of the mobile phase (100 mmol L^{-1} NaOH), which would affect seriously the performance of ICPMS measurements and exclude the use of other detectors (e.g. conductivity for Se-IV and Se-VI, amperometric for $SeCN^{-}$), they used a post-column membrane suppressor module (ASRS-II, 4 mm, Dionex).

In our work, we propose a new method that permits the efficient separation of Se(IV), Se(VI) and $SeCN^{-}$ in a relatively short time (<7 min) and without the need for step gradient elution and membrane suppression. The method uses a low conductivity, cyanuric acid-based mobile phase, suitable for the direct aspiration in ICPMS. Maurino and Minero [17] suggested cyanuric acid as a promising eluent for very strongly retained anions, such as those mentioned above. However, this reagent has never been tested for the separation of $SeCN^{-}$, which for structural reasons should behave very similarly as thiocyanate (SCN^{-}), neither for other