

Simultaneous separation and determination of Tl(I) and Tl(III) by IC-ICP-OES and IC-ICP-MS

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Abstract

A new hyphenated method was developed for the speciation of Tl. In this method, Tl(III) was complexed with DTPA to form a Tl(III)-DTPA anionic complex. Tl(I) did not form a complex with DTPA. The two species were separated simultaneously by means of ion chromatography using a Dionex cation exchange guard column, CG12A, and 15 mmol/l nitric acid as eluant. When ICP-OES was used as detector the detection limits for both species were 0.8 mg/l for an inert V-groove nebuliser and 0.1 mg/l for an ultrasonic nebuliser. No spectral interference was observed but high concentrations of metals such as Fe and Al could lead to broadening of the Tl(I) peak. It was demonstrated that the same chromatographic method can be used with ICP-MS detection. Detection limits were then reduced to 25 ng/l for Tl(I) and 70 ng/l for Tl(III).

Introduction

Tl and its compounds are used in various industrial applications such as semiconductors, nuclear medicine, catalysts, dyes and pigments, thereby increasing the risk of occupational poisoning and environmental pollution (Asami, 1996). It is also a byproduct in mercury mining. It is present in flue dust from coal-fired power stations and thus is being distributed in the environment. It is known that thallium is more toxic than Hg, Pb or Cd and is one of 13 priority metal pollutants listed by the USAEPA. Tl poisoning is therefore a recognised industrial hazard (Lin and Nriagu, 1999; Shabalina and Spiridonova, 1979), although not wide spread. Some unique applications of Tl are stimulating Tl related research in diverse fields ranging from toxicology (Borgmann, et al., 1998) and biology (Lepp and Logan, 1983) to chemistry (Kocovsky and Baines, 1993, Lin and Nriagu, 1999), and environmental monitoring. In these research fields the determination of the Tl(I) and Tl(III) species is important. In recent work in the environmental field (Lin and Nriagu, 1999), Tl(III), the more reactive form of Tl, was found to be the dominant Tl species in polluted waters of the Huron river. One must therefore assume that Tl(III) can be stabilised through complexation with ligands present in polluted river waters. Tl(III) forms very stable complexes with dicarboxylic acids and β -ketones. Depending on the application, the concentration levels at which the analysis must be performed span a wide range and can vary from mg/l in chemical research to ng/l in environmental monitoring.

During the last decade many analytical methods for Tl determination were developed, most of them focused on low level determinations in natural waters. Atomic absorption spectrometry (Ivanova et al, 1997), in particular ETA-AAS is widely used for the determination of Tl, due to its high sensitivity. Electrochemical methods (Bohrer and Schwedt, 1998; Kahlert et al, 1996 and Diewald et al, 1994), as well as spectrophotometric methods (Vartak and Shinde, 1998; Namboothiri et al, 1991; Mihajlovic and Stafilov, 1996 and Hafez et al, 1996) have also been used for Tl determination. In addition, fluorimetric methods (Perez-Ruiz et al, 1996), liquid scintillation counting (Rajesh and Subramanian,

1992 and 1994), and isotope dilution mass spectrometry (Oliver and Klaus, 1999) have been reported for Tl determination. However, these methods can determine only one of the two Tl species at a time (Lin and Nriagu, 1999 and Perez-Ruiz et al, 1996). Typically, one Tl species is measured, followed by the determination of total Tl concentration after oxidation or reduction. The other species concentration is then obtained by subtraction. Interference from other metals is a common problem in many published methods.

The aim of this work was to develop a quick, interference-free method for the simultaneous separation and determination of the two Tl species, Tl(I) and Tl(III). A hyphenated technique, IC-ICP-OES, i.e. ion chromatography (IC) coupled with inductively coupled plasma optical emission spectrometry (ICP-OES), or IC-ICP-MS, ion chromatography coupled with inductively coupled plasma mass spectrometry (ICP-MS) was developed for this purpose. This is the first useful IC-ICP-OES/MS method for the simultaneous online determination of Tl(I) and Tl(III) species.

Experimental

Apparatus

The IC-ICP-OES system consisted of a Dionex analytical pump (2000i), a Dionex cation exchange guard column, CG12A, and a Varian Liberty 110 ICP-OES spectrometer with V-groove nebuliser. The effluent from the column was fed directly into the nebuliser of the ICP-OES system. An ultrasonic nebuliser (Cetac, U-5000AT⁺) was used to enhance detection limits. The analog signal from the spectrometer was digitised and analysed using Varian Star Chromatography software (Version 4.0).

The IC-ICP-MS system consisted of a Waters Alliance 2690D high performance liquid chromatograph, a Dionex cation exchange guard column, CG12A, and a Micromass Platform ICP-MS (collision cell) with a V-groove nebuliser. Masslynx 3.4 software was used to control the instrument, to acquire, and to process data.

Reagents

A 1 000 mg/l Tl(I) stock solution was prepared by dissolving an appropriate amount of TlNO₃ (Seelze-Hannover) in deionised H₂O (18 M Ω). A 1 000 mg/l Tl(III) stock solution was prepared by

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