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Comparison between hydride generation and nebulization for sample introduction in the determination of lead in plants and water samples by inductively coupled plasma mass spectrometry, using external calibration and isotope dilution

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Abstract

Four inductively coupled plasma mass spectrometric methods: nebulization sample introduction with external calibration; hydride generation with external calibration; isotope dilution with nebulization; and isotope dilution with hydride generation, have been tested and compared. Multimode Sample Introduction System (MSIS™) was employed in either nebulization or hydride generation mode. Best limits of detection (below 0.1 μg L^{-1}) and accuracy were obtained for isotope dilution techniques in hydride generation and sample nebulization mode. A mixture of HNO_3 and H_2O_2 served both for microwave-assisted digestion as well as a medium for subsequent plumbane generation. Optimal reagent concentrations for hydride generation stage were 0.1 mol L^{-1} HNO_3, 0.28 mol L^{-1} H_2O_2 and 1.5% m/v $NaBH_4$. Critical effects of acidity, blanks and concomitants have been discussed. Analytical methods were validated by use of plant and water certified reference materials and spiked high-salt solutions (seawater and 20% m/v NaCl) at lead levels in nanograms per gram to micrograms per gram range.

Keywords: Lead; Isotope dilution; ICP-MS; Hydride generation; Plants; Water; Seawater

1. Introduction

This work has been mainly aimed at improving analytical performance of lead hydride generation (HG) by combining this approach for on-line separation and efficient analyte introduction with the most powerful current technique of analytical atomic spectrometry, inductively coupled plasma mass spectrometry (ICP-MS) with isotope dilution (ID) [1], i.e. evaluating the HG-ID-ICP-MS and nebulization-ID-ICP-MS vs. HG-ICP-MS and ICP-MS with external calibration in analysis of some difficult environmental samples and certified reference materials (CRMs) such as plant digests, sea water and 20% m/v NaCl brines. To our best knowledge, the HG-ID-ICP-MS technique for Pb seems to have been reported only once in the early paper by Wang et al. [2] and abandoned afterwards, which is in apparent contrast with the environmental, occupational and toxicological importance of lead and its popularity as one of the most abundant and frequently determined heavy metals [3–6].

Lead is an ubiquitous, nonessential toxic trace element [7,8] with cumulative effects and relatively long biological half-time. Its concentration in biological and environmental samples is spread within a broad interval of 7–8 orders of magnitude [3,7,8]: from low nanograms per liter in aquatic samples such as open ocean and unpolluted seawater; from sub-micrograms per liter to around a few micrograms per liter in some biological fluids and drinking water; and from sub-micrograms per gram to a few micrograms per gram in unpolluted plant tissues, with somewhat higher levels in leafy vegetables and

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forages. Some of these matrices are challenging for the ICP-MS technique because of their high organic matter and total dissolved solids as well as the presence of numerous potential interferents on processes of vapor generation and ICP-MS determination.

Chemical vapor generation (mostly hydride generation) is a well known method for sample introduction, enrichment and matrix separation in atomic spectroscopy, as reviewed recently [9–12]. Plumbane (PbH_4) generation, first introduced by Thompson and Thomerson [13] three decades ago, has not yet become a straightforward and popular technique in contrast to HG for As, Se, Sb, Sn, Bi and Te. Recent reviews [12–14] and monograph [15] summarize difficulties and problems with lead HG: relatively narrow pH interval for reaction; critical effect of the oxidant (kind, concentration, reaction time) [16]; low chemical yield of HG reaction [17], presence of metal ions, catalyzing or inhibiting reaction or otherwise decomposing and retaining the generated hydride; vigorous reactions entailing foaming and aerosol formation; ambiguous effects of various complexing and masking agents [18]. Due to these problems most manufacturers do not recommend their hydride generators for Pb.

In early HG atomic absorption spectrometric study, Bonilla et al. [19] observed increase in plumbane generation by high amounts of alkali metals (Na, K, Ca, Sr), while Ni, Co and Mn served as catalysts of PbH_4 generation. Aroza et al. [20] considered Ni as catalyst when applied in small amounts to biological digests. Similar results were obtained in the same laboratory for Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} which exhibited positive effects on HG [21]. On the contrary, Wang et al. [2] found signal decrease in the presence of Mn^{2+}, Ni^{2+}, Cu^{2+} and Fe^{3+}.

Plumbane generation is vulnerable to complex effects which are poorly understood and hard to control. Regardless of kinetic role of interferent (catalyst or inhibitor) it changes the signal intensity of the sample compared to the standard with the same concentration. Absolute signal change in HG-ID-ICP-MS does not affect isotope ratio and therefore this technique is expected to ensure trace lead determinations with higher metrological value.

In principle, the isotope dilution is simple; the change of signal intensity ratio for two selected isotopes is measured after addition of a known quantity spike enriched in one of the isotopes (for elements with invariable isotope abundance). However, in practice there are several considerations — mass bias, detector dead time and spectral overlapping from isobars and molecular ions (polyatomic ions). Additional attention should be paid to elements with variable isotope composition. ID is of special interest for complex matrices where serious interferences are expected. The use of HG-ID-ICP-MS is expected to solve many of the aforementioned problems with plumbane generation. In this work, performance of four ICP-MS methods was tested and compared: two sample introduction modes, nebulization (Neb) and HG in combination with external calibration and ID: Neb-ICP-MS, Neb-ID-ICP-MS, HG-ICP-MS, and HG-ID-ICP-MS.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer SCIEX (Norwalk, CT, USA) Elan 5000 Inductively Coupled Plasma Mass Spectrometer with Discrete Dynode Multiplier detector, equipped with ELAN 5000 XENIX operating software was used. The samples were introduced using the Multi Mode Sample Introduction System (MSIS™) [22–24] with Burgener Mira Mist™ parallel path nebulizer (Burgener Research International, Berkshire, UK) and a Gilson — 10 rolls, 4 channels peristaltic pump (Paris, France). Peristaltic pump tubing was: sample channel — Elkay Accurate Tubing (Black/Black; Lot No. x2785; Elkay Eirean, Costelloe, Co. Galway); reduction channel — Elkay Accurate Tubing (Yellow/Yellow; Lot No. t20045); drain channel — Tyco/Healthcare (0.125″ i.d.; Black/White; Type: Standard). The MSIS™ was connected via rubber tubing to the inlet of ICP-MS torch. A schematic drawing of the sample introduction system is shown in Fig. 1. The MSIS™ can be used in three different modes: (*i*) conventional pneumatic nebulization, (*ii*) HG and (*iii*) the combination of HG and liquid nebulization (dual mode). In this work only single mode operations were used, i.e. the HG and nebulization mode were operated sequentially. Dotted lines in Fig. 1 show the inlet channels for HG mode (on the top of MSIS™ chamber) and tangentional nebulization (from aside of the MSIS™ chamber). To avoid problems with plasma ignition (probably because of entraining air), the entrance holes not in use in single mode operation were blocked, viz.: either entrance holes for sample (inlet on the top of the chamber) and reductant solution were closed during nebulization mode or the nebulizer channel (inlet on the side) was sealed in HG mode of operation.

Milestone Microwave Laboratory System ETHOS 1600 — Advanced Microwave Labstation equipped with Easywave software Version 3.1.3.0 (Sorisole, Italy) was used for pressurized sample decompositions in 100 mL TFA Teflon

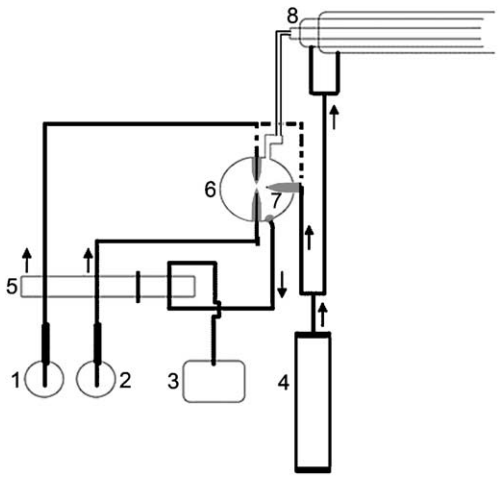

Fig. 1. Schematic diagram of the sample introduction system. The arrows show direction of flows. 1 — sample container; 2 — reductant container; 3 — drain container; 4 — Ar gas bottle; 5 — peristaltic pump; 6 — MSIS chamber; 7 — Mira Mist nebulizer; 8 — ICP torch.