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Simultaneous generation of hydrides of bismuth, lead and tin in the presence of ferricyanide and application to determination in biominerals by ICP-AES†,‡

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Abstract

Performance of potassium ferricyanide, $K_3Fe(CN)_6$, for simultaneous generation of hydrides of Bi, Pb and Sn in dilute HCl is investigated for determination by ICP-AES. On-line addition of $K_3Fe(CN)_6$ to sample solution was essential to achieve optimum signals and stability in generation of BiH_3 and SnH_4 . Off-line addition caused instability for $Bi_{(m)}$ and $Sn_{(iv)}$ that resulted in substantial loss in hydride generation efficiency within 24 h. Lead hydride (PbH_4) generation, however, was not influenced from on-line or off-line addition of $[Fe(CN)_6]^{3-}$, nor did it show any instability under the same conditions indicating that $[Fe(CN)_6]^{3-}$ affects generation of PbH_4 differently from those of BiH_3 and SnH_4 . The effects of transition metals and hydride forming elements were not significant, except $Cr_{(vi)}$ and $Cu_{(ii)}$ that suppressed the signals of Bi and Sn, and Pb, respectively, at and above $1.0 \mu g mL^{-1}$. The detection limits ($3s, n = 11$) were 0.20, 0.13 and $0.10 \mu g L^{-1}$ for Bi, Pb and Sn, respectively. The method was applied to the analysis of calcium-rich biominerals - fish otoliths and NIST bone ash certified reference material (SRM 1400).

Introduction

Hydride generation (HG) is a popular sample introduction method in atomic spectroscopy including plasma source emission spectroscopy to enhance sensitivity in determination of hydride forming elements, such as As, Bi, Pb, Se, and Sn, at trace levels.^{1–9} Determination of Pb by HG has been described in various papers.^{10–15} Lead hydride (PbH_4 , plumbane) is generated from $Pb_{(iv)}$ oxidation state in the presence of oxidizing agents, such as potassium ferricyanide, $K_3Fe(CN)_6$,^{11–14} which has been among the most effective reagents for generation of plumbane. While the role ferricyanide in PbH_4 generation is usually explained by oxidation of $Pb_{(ii)}$ to $Pb_{(iv)}$, it was reported that enhancement could be obtained without interaction of $Fe[(CN)_6]^{3-}$ with $Pb_{(ii)}$.¹⁶ The phenomenon was explained by formation of hydroboron species in the presence of $Fe(CN)_6^{3-}$ that react efficiently with $Pb_{(ii)}$ to generate plumbane. In another paper, oxidizing agents, including $Fe[(CN)_6]^{3-}$, $Fe_{(iii)}$, KSCN, $Mo_{(iv)}$, and $KMnO_4$ were found to facilitate the generation of bismuthane (BiH_3), where the effect was described by stabilization of $Bi_{(m)}$ in solution through formation of reactive species that prevent formation of $Bi(0)$.¹⁷

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The use of $\text{K}_3\text{Fe}(\text{CN})_6$ for multielement determination by HG has been reported only recently.¹⁸ Though $\text{K}_3\text{Fe}(\text{CN})_6$ appears to be a versatile reagent for multielement hydride generation, performance characteristics under different conditions and matrices are not fully understood yet. In this paper, we investigated the role and performance of $\text{K}_3\text{Fe}(\text{CN})_6$ by adding to test solutions in off-line and on-line manner for generation of hydrides of Bi, Pb and Sn for determination by ICP-AES. Experimental conditions, including sample acidity, $\text{K}_3\text{Fe}(\text{CN})_6$ and NaBH_4 concentration, flow rates of sample and carrier gas were examined on the signal intensity. Interferences from the transition metal ions and other hydride forming elements were also investigated.

Experimental

Reagents and solutions

Deionized water produced by Barnstead™ E-Pure system with minimum resistivity of 17.1 MΩ cm was used throughout. A 10 µg mL⁻¹ multielement standard solution was prepared from a 1000 µg mL⁻¹ single element standard solutions (SPEX Certiprep) and stored in 2% v/v HNO_3 (Trace metal grade, Fisher Scientific). Tin (Sn) standard solution (10 µg mL⁻¹) was prepared from 1000 µg mL⁻¹ Sn standard solution (SPEX Certiprep) and stored in 2% v/v HCl (Trace metal grade, Fisher Scientific). All experimental solutions and calibration standards were prepared by one-stage dilution from these stock standard solutions. Potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$, 99%+) and sodium borohydride (NaBH_4 , 98%) were purchased from Sigma Aldrich. Potassium ferricyanide solution was prepared by dissolving the appropriate amount in water. Sodium borohydride solution was prepared daily in 0.1% m/v NaOH solution.

Instrumentation

A PerkinElmer (Shelton, CT, USA) Optima 3300 DV ICP-AES instrument was used throughout the course of the experiments. The instrument is optimized for sensitivity with 2 µg mL⁻¹ Mn solution as needed. Data collection was achieved by ICP-WinLab software package (version 1.42). Measurements were made in axial view mode using recommended wavelengths. The operating parameters of the instrument are summarized in Table S1 (ESI†). A laboratory made quartz gas-liquid separator (GLS) with inner volume of 60 mL was used. The schematic diagram of the hydride generation manifold and the GLS are illustrated in Fig. 1. Tygon pump tubings were used for sample (1.52 mm i.d., yellow/blue), $\text{K}_3\text{Fe}(\text{CN})_6$ and NaBH_4 (0.76 mm i.d., black/black). The waste line running on a separate peristaltic pump (Ismatec) was made up of two tygon tubings (2.79 mm i.d., purple/white). Connection tubings between the sample and reagent lines were 0.8 mm i.d. PTFE, while the reaction coil (e.g., transfer line) was 1.14 mm i.d., (red/red) tygon tubing. The GLS was connected to the injector tube adaptor by means of polyethylene elbow (4 mm i.d.). The instrument was run in the hydride generation settings for about 30 min each day before collecting any data.

Sample preparation

Two different biominerals, fish otolith and bone ash, were used for method validation. Fish otoliths collected from adult Pacific Halibut were kindly provided by NOAA James Howard Marine Laboratory, Sandy Hook NJ. Bone Ash (SRM 1400) was purchased from National Institutes of Standards and Technology, Gaithersburg, MD. Fish otoliths are made up of mainly CaCO_3 in the aragonite polymorph. Bone ash (SRM 1400) is purely calcium phosphate produced from calcinations of bone. Digestions of the otolith and bone ash were carried out similarly as described elsewhere for otoliths.¹⁹ Approximately 0.25 g sub-samples were placed in teflon tubes (60 mL) and digested in 2 mL HNO_3 until dryness at 150 °C using a digestion block (Digi Prep MS, SCP Science). Digestion was repeated with additional 1 mL HNO_3 to effectively oxidize the protein matrix, especially for otoliths. Following the dissolution, the contents in tubes were evaporated to dryness and the residue was rinsed with about 1 mL water

twice and then heated to dryness again. The residue was then dissolved and completed to 15 mL with 0.75% v/v HCl.

Results and discussion

Effects of off-line and on-line addition of $\text{K}_3\text{Fe}(\text{CN})_6$ on hydride generation

Initially, appropriate volumes of 20% m/v $\text{K}_3\text{Fe}(\text{CN})_6$ in water was added off-line to 50 $\mu\text{g L}^{-1}$ multielement solutions in 0.5% v/v HCl to yield concentrations between 0 and 2% m/v, which were then reacted on-line with 1% m/v NaBH_4 . Signals profiles gathered from the same solutions within 1 h and 24 h are illustrated in Fig. 2a and 2b, respectively. Plumbane generation improved rapidly with increasing $[\text{Fe}(\text{CN})_6]^{3-}$ concentration and signals remained relatively stable over 24 h (Fig. 2b). For Bi and Sn, $[\text{Fe}(\text{CN})_6]^{3-}$ improved the generation of BiH_3 significantly and that of SnH_4 to some extent in fresh solutions (Fig. 2a). However, the signals for these elements tended to decrease in time as manifested by a drastic loss when the same solutions were reanalyzed after 24 h (Fig. 2b). This behavior suggested that $\text{Bi}_{(\text{III})}$ and $\text{Sn}_{(\text{IV})}$ were unstable in acidic $[\text{Fe}(\text{CN})_6]^{3-}$ medium. D'Ulivo *et al.*¹⁷ reported similar enhancement of BiH_3 generation in the presence of $[\text{Fe}(\text{CN})_6]^{3-}$ supporting the results in this study. However, it should be noted that off-line addition of $[\text{Fe}(\text{CN})_6]^{3-}$ is not suitable for quantitative determination of Bi and Sn since HG efficacy deteriorates substantially with increasing periods of time from addition of $[\text{Fe}(\text{CN})_6]^{3-}$ to the analysis.

In on-line addition of $[\text{Fe}(\text{CN})_6]^{3-}$, a series of $[\text{Fe}(\text{CN})_6]^{3-}$ solutions prepared in water were introduced on-line to a stream of 50 $\mu\text{g L}^{-1}$ multielement solution in 0.5% v/v HCl using the manifold shown in Fig. 1. The solutions were mixed along a 80-cm long teflon tubing and then reacted with 1% m/v NaBH_4 solution. Signal profiles are illustrated in Fig. 3. As in the off-line mode, 1% m/v $\text{K}_3\text{Fe}(\text{CN})_6$ enhanced PbH_4 generation substantially. Stability and precision were better at around 2.5–3% m/v. Signals for Bi were also improved by about a factor of two and were better than those with off-line approach. Enhancement was also noted for Sn for which signals were comparably higher and more stable than observed in off-line experiments (see Fig. 2a).

Potassium ferricyanide is a mild oxidizing agent with a relatively small reduction potential, $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ ($E^\circ = 0.358 \text{ V}$). The experimental results from off-line and on-line approaches demonstrate that $[\text{Fe}(\text{CN})_6]^{3-}$ acts as an oxidizing agent in the formation of BiH_3 and SnH_4 from $\text{Bi}_{(\text{III})}$ and $\text{Sn}_{(\text{IV})}$. Though fresh $[\text{Fe}(\text{CN})_6]^{3-}$ exhibits sufficient stabilization on $\text{Bi}_{(\text{III})}$ and $\text{Sn}_{(\text{IV})}$, instability occurs in prolonged times due to the slow reduction of Bi^{3+} to Bi^+ ($E^\circ = 0.2 \text{ V}$) and Sn^{4+} to Sn^{2+} ($E^\circ = 0.151 \text{ V}$). It was also noted that the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ was faster in acidic sample solution in the presence metal ions so that bright yellow color of $[\text{Fe}(\text{CN})_6]^{3-}$ changed to dark green/blue color of $[\text{Fe}(\text{CN})_6]^{4-}$ overnight. In water, however, $[\text{Fe}(\text{CN})_6]^{3-}$ solution was stable for weeks without any change in its color. Based on this, it can be stated that the abovementioned instability for $\text{Bi}_{(\text{III})}$ and $\text{Sn}_{(\text{IV})}$ was mainly associated with the instability of $[\text{Fe}(\text{CN})_6]^{3-}$ resulting in inadequate oxidizing conditions.

Under similar conditions, Pb is also expected to be reduced to Pb^{2+} because of the large reduction potential ($\text{Pb}^{4+}/\text{Pb}^{2+}$ $E^\circ = 1.69 \text{ V}$). Likewise, the effect would be manifested by reduction in HG efficacy after 24 h as for Bi and Sn. The stable patterns of Pb signals in fresh and aged solutions (Fig. 2a and 2b), however, demonstrate that formation of PbH_4 was not affected from the oxidation state of Pb. This result is also in agreement with that of D'Ulivo *et al.*¹⁶ and in due course verifies that $[\text{Fe}(\text{CN})_6]^{3-}$ assists in PbH_4 generation *via* formation of reactive intermediates that facilitate formation of PbH_4 .

Effects of HCl and NaBH₄ concentration

The effect of HCl concentration on the signals of the elements is illustrated in Fig. 4 for a 50 µg L⁻¹ multielement solution. For all three elements, optimum signals were obtained within a range from 0.5 to 1% v/v HCl. The range was relatively broad for BiH₃ and SnH₄ ranging from 0.5% v/v to 1.5% v/v HCl, but that for PbH₄ was relatively narrow characterized with a maximum at around 0.75% v/v HCl. This behavior was also reported in previous papers that efficiency in plumbane generation is highly influenced by the acid concentration of medium.^{11,12,14} The acidity of the solutions was adjusted to 0.75% v/v HCl throughout the rest of the experiments.

The effect of NaBH₄ solution on HG was examined using a series of NaBH₄ solutions between 0 and 3% m/v NaBH₄ prepared in 0.1% m/v NaOH. For BiH₃ and SnH₄, 1% m/v NaBH₄ was satisfactory to achieve maximum signals, whereas PbH₄ generation occurred with higher concentrations at around 2% m/v. Plasma stability deteriorated for levels greater than 2.5% m/v NaBH₄ because of increasing water vapor reaching to the plasma which could not be maintained for NaBH₄ levels greater than 3% m/v.

Effects of flow rates of carrier argon, sample solution and length of reaction line

The nebulizer argon (carrier gas) flow rate varied from 0.3 to 0.75 L min⁻¹ to affect the signals. Optimum gas flow rate was around 0.45 L min⁻¹. Signals declined with flow rates greater than 0.55 L min⁻¹ which is due to the shift in the observation distance in the plasma. The length of the reaction coil (RC, see Fig. 1) was increased up to 30 cm. It was found that hydrides of the elements were successfully generated even by using a 5-cm long tubing. The length of the line was adjusted to 10 cm to maintain stability. Signals also increased with increasing sample flow rate of the solution up to 6 mL min⁻¹. Further increase did not provide any significant enhancement. The precision was better (*e.g.*, RSD < 4%) with higher flow rates because of the higher mass transport into the plasma.

Analytical performance

Under the optimum conditions, the detection limits (3s, *n* = 11) were 0.20, 0.13, 0.10 µg L⁻¹ for Bi, Pb and Sn, respectively. Detection limits for Pb were limited by relatively higher blank signals, mainly because of the impurities in potassium ferricyanide. Precision was 5.2% and 1.4% RSD (*n* = 5) at 2 and 50 µg L⁻¹ levels, respectively. Calibration was performed with multielement solutions (0, 1, 2, 5, 10, 20 and 50 µg L⁻¹) in 0.75% v/v HCl. Calibration curves for the elements were linear (*r*² = 0.995–1.00). In comparison of the detection limits from this study with those of conventional ICP-AES, the method has afforded an improvement in sensitivity of at least two orders of magnitude.

The interferences from transition metal ions and other hydride forming elements, including Ag (I), As (III), Cd (II), Co (II), Cr (VI), Cu (II), Mn (II), Ni (II), Sb (III), Se (IV) and Zn (II), were studied for 1.0 µg mL⁻¹ of each individual element, and 10, 100 and 1000 µg mL⁻¹ solutions of Al, Mg and Ca, respectively. No significant interferences were observed from the transition metal ions, except those from Cr (VI) and Cu (II). Suppression was noted on Bi and Sn by Cr (VI) and on Pb by Cu (II), for which effects were alleviated at 0.25 µg mL⁻¹ levels and below. Hydride forming elements (As, Cd, Sb and Se) did not cause any significant interference on any of the analyte element, nor did Al (III), Mg (II) and Ca (II) at the concentrations added to the solutions.

Application to fish otoliths and bone ash

The results obtained from the analysis of fish otolith and bone ash (SRM 1400) samples are summarized in Table 1 along with indicative values from ICP-MS measurements. A series of samples from the powdered material were spiked with known concentrations of the elements

and digested along with the unspiked samples in HNO₃ as described above. The otoliths solutions contained about 0.65% m/v Ca²⁺ (as nitrate) that was six-fold higher than the concentration tested during interference studies. The elemental concentrations (Table 1) were similar to those reported previously.¹⁹ The accuracy achieved for the spiked samples demonstrates that the method is not affected from higher levels of Ca²⁺ and consequently offers accurate determination of Bi, Pb and Sn simultaneously in otoliths.

Total calcium content in bone ash solutions was also around 0.65% m/v, but in the form of calcium hydrogen or dihydrogen phosphate. The results for Bi and Pb were quantitative indicating that the optimized HG method affords accurate determination of Bi and Pb under high levels of calcium and phosphates. Interestingly, Sn could not be measured in solutions of the bone ash, nor in those that contained 10 µg L⁻¹ Sn spike despite successful measurements in otoliths. The signals for Sn were almost same with those of the blank solutions (*ca.* 100–250 cps), which is difficult to explain by matrix-induced suppression or inhibition of SnH₄ generation only. A careful examination of bone ash matrix revealed that this material contains substantial levels of fluorine (*ca.* 1250 µg g⁻¹). Fluorides of both Sn(II) and Sn(IV) exhibit volatility, which consequently suggests Sn was most likely lost as tin fluoride during the sample dissolution since the samples were dried several times to eliminate excess HNO₃ before adjusting the acidity with 0.75% v/v HCl.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Fig. 1.

Hydride generation manifold. Sample acidity = 0.75% v/v HCl; $\text{K}_3\text{Fe}(\text{CN})_6$ = 3% m/v in water; NaBH_4 = 1% m/v in 0.1% NaOH. MC (mixing coil) = 80-cm PTFE tubing (0.8 mm i.d.); RC (reaction coil) = 10-cm Tygon tubing (1.14 mm i.d.).

Fig. 2. Signal profiles for Bi, Pb and Sn when $K_3Fe(CN)_6$ is added to $50 \mu g L^{-1}$ multielement solution in 0.5% v/v HCl. (a) within 1 h of preparation; (b) reanalysis of the same solutions after 24 h.

Fig. 3. Signal profiles for Bi, Pb and Sn when $K_3Fe(CN)_6$ is mixed on-line with $50 \mu g L^{-1}$ multielement solution in 0.5% v/v HCl.

Fig. 4. The effect of HCl concentration on the signals of Bi, Pb and Sn from $50 \mu\text{g L}^{-1}$ multielement solutions mixed on-line with 3% m/v $\text{K}_3\text{Fe}(\text{CN})_6$ solution.

The results for Bi, Pb and Sn from analysis of fish otolith and bone ash samples (SRM 1400) by hydride generation procedure. Results are given as mean $\pm$ standard deviation ($n = 4$). Spiked samples contained $1.0 \mu\text{g g}^{-1}$ of each element added prior to digestion. Values in parenthesis are indicative values for the same sample solutions by ICP-MS. Certified value of Pb in Bone Ash (SRM 1400) is $9.07 \pm 0.12 \mu\text{g g}^{-1a}$

Table 1

	Fish otolith		Bone ash		LOD/ $\mu\text{g L}^{-1}$
	Unspiked/ $\mu\text{g g}^{-1}$	Spiked/ $\mu\text{g g}^{-1}$	Unspiked/ $\mu\text{g g}^{-1}$	Spiked/ $\mu\text{g g}^{-1}$	
Bi	0.02 ± 0.01 (0.03 ± 0.01)	0.91 ± 0.10	0.02 ± 0.01 (0.015 ± 0.01)	0.91 ± 0.02	0.2
Pb	0.07 ± 0.02 (0.08 ± 0.01)	0.98 ± 0.14	8.44 ± 0.37 (8.60 ± 0.40)	8.92 ± 0.56	0.13
Sn	0.19 ± 0.04 (0.14 ± 0.06)	1.0 ± 0.1	nd (<0.05)	nd	0.1

^a nd = not detected.