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Determination of lead by hydride generation inductively coupled plasma mass spectrometry (HG-ICP-MS): on-line generation of plumbane using potassium hexacyanomanganate(III)

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Abstract

A hydride generation (HG) procedure has been described for determination of Pb by ICP-MS using potassium hexacyanomanganate(III), $K_3Mn(CN)_6$, as an additive to facilitate the generation of plumbane (PbH_4). Potassium hexacyanomanganate(III) was prepared in acidic medium as it was unstable in water. The stability of hexacyanomanganate(III) was examined in dilute solutions of HCl, HNO_3 and H_2SO_4 . The solutions prepared in 1% v/v H_2SO_4 were found to be stable for over a period of 24 h. The least suitable medium was 1% v/v HNO_3 . For generation of plumbane, acidic hexacyanomanganate(III) and sample solutions were mixed online along a 5-cm long tygon tubing (1.14 mm i.d.) and then reacted with 2% m/v sodium borohydride ($NaBH_4$). A concentration of 0.5% m/v $K_3Mn(CN)_6$ facilitated the generation of PbH_4 remarkably. In comparison to H_2SO_4 , HCl provided broader working range for which optimum concentration was 1% v/v. No significant interferences were noted from transition metals and hydride forming elements, up to $0.5 \mu g mL^{-1}$ levels, except Cu which depressed the signals severely. The depressive effects in the presence of $0.1 \mu g mL^{-1}$ Cu were alleviated by increasing the concentration of $K_3Mn(CN)_6$ to 2% m/v. Under these conditions, the sensitivity was enhanced by a factor of at least 42 to 48. The detection limit (3s) was $0.008 \mu g L^{-1}$ for ^{208}Pb isotope. Average signal-to-noise ratio (S/N) ranged between 18 and 20 for $1.0 \mu g mL^{-1}$ Pb solution. The accuracy of the method was verified by analysis of several certified reference materials, including Nearshore seawater (CASS-4), Bone ash (SRM 1400), and Mussel tissue (SRM 2976). The procedure was also successfully applied to the determination of Pb in coastal seawater samples by ICP-MS.

Keywords

Lead; Hydride generation; Hexacyanomanganate(III); ICP-MS

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1. Introduction

Hydride generation (HG) has been realized as one of the most powerful analytical tools in atomic spectrometry despite the fact it is applicable to the determination of a small number of elements, including As, Bi, Pb, Sb, Se, Sn, and Te that form covalent hydrides at ambient conditions [1–9]. The advantages of the HG are mainly due to the more efficient transport of gaseous sample to the excitation or atomization source. In comparison to conventional solution nebulization, sensitivity could be boosted as high as two orders of magnitude for certain hydride forming elements, such as As, Se and Te that exhibit poor atomization and excitation.

Generation of lead hydride (PbH_4 , plumbane) was reported first by Thompson and Thomerson [10] about four decades ago. Numerous papers have been published since then to improve the analytical figures of merit (selectivity, sensitivity, detection limit and precision) for determination of Pb by hydride generation [11–26]. It has been well documented now that generation of plumbane is more sensitive to acidity of the medium than hydrides of other elements. In addition to relatively narrow range of acidity, difficulties are associated with, efficiency of oxidizing agents, instability of plumbane, and interferences of transition metals and hydride forming elements. Plumbane is assumed to be generated from the Pb(IV) oxidation state of Pb. Therefore, various oxidizing agents have been utilized in most studies to oxidize Pb(II) to Pb(IV) in acidic solutions. These include hydrogen peroxide [18–22], ammonium or sodium persulfate [19,23,24], potassium dichromate [19,21], ammonium cerium (IV) nitrate [25,26]. The use of chelating agents is rather scarce. Chen et al. [27] reported that a number of chelating agents, including nitroso R salt, Bromo pyrogallol red, Pyrocatechol violet, Alizarine red-S, 5-Br-PADAP and PAN-S enhanced signals in determination of Pb by hydride generation. Contrary to the scenario with oxidizing agents, their results suggested that plumbane could also be generated directly from the chelated Pb(II).

Potassium hexacyanoferrate(III) ($\text{K}_3\text{Fe}(\text{CN})_6$) was first used in determination of Pb by hydride generation atomic spectrometry in 1985 [28]. It is by far the most effective reagent to date in generation of plumbane in acidic solutions; consequently, it has become inevitable for determination of Pb by hydride generation using various spectrometric techniques [12–17, 29–34]. As a mild oxidizing agent, its action in plumbane generation was attributed to the oxidation of Pb(II) to Pb(IV) although the reduction potential ($E^\circ = 0.36 \text{ V}$) of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ is much lower than that required for oxidation of Pb^{2+} to Pb^{4+} ($E^\circ = -1.69 \text{ V}$). This assumption has been disproved recently that plumbane was generated as efficiently as even if $[\text{Fe}(\text{CN})_6]^{3-}$ was not interacted directly with Pb(II) in the solution prior to reaction with NaBH_4 [31]. In another study, generation of plumbane was not affected from the reduction of $[\text{Fe}(\text{CN})_6]^{3-}$ to $[\text{Fe}(\text{CN})_6]^{4-}$ such that trace amounts of $[\text{Fe}(\text{CN})_6]^{3-}$ was sufficient for formation of PbH_4 [17]. The effectiveness of hexacyanoferrate(III) was explained by the formation of reactive intermediates, such as hydroboranes, facilitating the generation of PbH_4 .

Transition metals form complex cyanides that possess different thermodynamic and catalytic properties. Only a few of these cyanide complexes are stable (e.g., Fe, Ag and Au), and hence, they have not been considered as an additive in hydride and vapor generation approaches apart from the most popular hexacyanoferrate(III). In a recent paper, we have demonstrated that hexacyanochromate(III) could facilitate the generation of Cd vapor allowing better sensitivity and selectivity to be achieved in determination of Cd [35]. In this paper, we have investigated the performance of a new transition metal cyanide complex, potassium hexacyanomanganate(III) ($\text{K}_3\text{Mn}(\text{CN})_6$), for generation of plumbane and described a highly sensitive and robust method for determination of Pb by hydride

generation. Plumbane was generated by interacting Pb(II) in acidic solution with $K_3Mn(CN)_6$ followed by reaction with sodium borohydride ($NaBH_4$). The gaseous hydride was transported rapidly to argon plasma of ICP-MS through a cooled spray chamber. The effects of solution acidity, concentrations of $K_3Mn(CN)_6$ and $NaBH_4$, and the manifold parameters were optimized. The tolerance of the method to chemical interferences of transition metals and hydride forming elements was investigated. The method was applied to the determination of Pb in various certified reference materials and samples of coastal seawater by ICP-MS.

2. Experimental

2.1. Materials and solutions

All solutions were prepared with double deionized water (18 M Ω cm resistivity) obtained from a Barnstead E-Pure system fed by a reverse-osmosis system (SpectraPure). A 1.0 $\mu\text{g mL}^{-1}$ Pb standard solution was prepared from a 1000 $\mu\text{g mL}^{-1}$ stock solution (SPEX Certiprep, Metuchen, NJ) and stored in 1% v/v HNO_3 (Trace metal grade, BDH Chemicals). All experimental solutions and calibration standards were prepared from this solution. Solutions of the other trace elements, including As, Bi, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Na, Ni, Sb, Se and Zn, were either prepared from high-purity salts or from 1000 $\mu\text{g mL}^{-1}$ stock solutions (Spex Certiprep). Sodium borohydride ($NaBH_4$, 98%) was purchased from Sigma Aldrich, St. Louis, MO. Sodium borohydride ($NaBH_4$) solution was prepared daily in 0.1% m/v sodium hydroxide ($NaOH$, Fisher Scientific). Hydrogen peroxide (H_2O_2 , 99.999%, Sigma Aldrich) was used along with HNO_3 in digestion of tissue samples.

Potassium hexacyanomanganate(III) ($K_3Mn(CN)_6$, reagent grade) was obtained from MP Biomedicals, Solon, OH (Lot No: 41218). It was prepared in 1% v/v H_2SO_4 (trace metal grade, Fisher Scientific). Lead impurities were removed from $K_3Mn(CN)_6$ solutions by coprecipitation of Pb(II) with calcium fluoride (CaF_2). Detailed information about the cleaning procedure is provided below using ammonium fluoride (NH_4F) and calcium nitrate solutions. Ammonium fluoride (NH_4F , electronics grade, 40% m/v, $\sim 12 \text{ mol L}^{-1}$) was purchased from Sigma Aldrich. Calcium nitrate solution was prepared by dissolving 2.5 g of ultrapure $CaCO_3$ (99.99%, Alfa Aesar) slowly with 20% v/v HNO_3 and completed to 20 mL with water yielding 50 mg mL^{-1} Ca(II) (as nitrate). The HNO_3 solution was added incrementally during dissolution of $CaCO_3$ to obtain a neutral to slightly acidic $Ca(NO_3)_2$ solution. The solution was heated briefly to convert carbonates to carbon dioxide.

2.2. Instrumentation and hydride generation manifold

Measurements were performed by using a Varian 820MS ICP-MS instrument (Varian, Australia). The instrument was equipped with a peltier-cooled double-pass glass spray chamber, standard one-piece low flow ball-and-socket connection quartz torch, standard Ni sampler and skimmer cones, and all-digital discrete dynode electron multiplier detector. The instrument was optimized daily in nebulization mode for sensitivity, doubly charged ions (<2%) and oxides (<3%) with 5 $\mu\text{g L}^{-1}$ solution of ^{138}Ba , ^{25}Mg , ^{115}In , ^{140}Ce , ^{208}Pb . Samples were introduced manually to the instrument. Data were collected by ICP-MS Expert software package (version 2.2 b126) at peak hopping mode using the ^{206}Pb , ^{207}Pb and ^{208}Pb . The operating parameters of the instrument are summarized in Table 1.

Schematic diagram of the hydride generation manifold is illustrated in Fig. 1. The stand-alone spray chamber with 100 mL inner volume was used as gas-liquid separator. The pneumatic nebulizer (Ari-mist) was removed and a polypropylene T-piece (4.0 mm id) was installed as shown in Fig. 1. Carrier argon was introduced by means of the T-piece inserted to the inlet of the spray chamber. Its flow rate was controlled by tuning the flow rate of the nebulizer argon gas. Tygon peristaltic pump tubings were red/red stop (1.14 mm i.d.) for

sample and NaBH_4 , and black/black stop (0.76 mm i.d.) for $\text{K}_3\text{Mn}(\text{CN})_6$. The waste line was on a separate peristaltic pump utilizing a purple/white stop tygon tubing (2.79 mm i.d.). The reaction coil was 5.0 cm long tygon tubing (1.14 mm i.d.). The transfer line was 20 cm long PTFE tubing (1.6 mm i.d.) which was extended into the spray chamber through the T-piece (Fig. 1). Other lines used for connections were made of 0.8 mm i.d. PTFE tubing. Sample solutions in 1% v/v HCl were pumped at 1.0 mL min^{-1} and mixed on-line with 2% m/v $\text{K}_3\text{Mn}(\text{CN})_6$ solution in 1% v/v H_2SO_4 running at 0.5 mL min^{-1} . This mixture was then reacted with 2% m/v NaBH_4 pumped at a flow rate of 1.0 mL min^{-1} .

2.3. Preparation and cleaning of potassium hexacyanomanganate(III) solution

Potassium hexacyanomanganate(III) was unstable in water, therefore, the experimental solutions could not be prepared in water. Further, the reagent grade chemical was found to contain significant Pb impurity. A cleaning procedure was developed based on the co-precipitation of Pb impurities with CaF_2 according to the procedures described elsewhere [36]. A 6% m/v $\text{K}_3\text{Mn}(\text{CN})_6$ solution was prepared in 2% v/v H_2SO_4 by dissolving 0.6 g of the reagent in 10 mL of 2% v/v H_2SO_4 . The reagent was placed into a dry 15-mL tube and dissolved by adding 2% v/v H_2SO_4 solution (ca. 8 mL) directly onto the reagent. Dissolution was relatively slow. Therefore, the contents were vortexed repeatedly yielding a deep-red solution in about 4–5 min. The volume was completed to 10 mL with 2% v/v H_2SO_4 solution. Care should be given to avoid contact with water as it results in loss of reagent even after the solution is acidified. It should be noted that contact with water does not deteriorate the stability of the solution once the solid reagent is successfully dissolved in acidic solution.

The 6% m/v $\text{K}_3\text{Mn}(\text{CN})_6$ stock solution was pipetted as 1.0 mL portions into 2-mL micro-centrifuge tubes. To each tube, first 0.1 mL of $12 \text{ mol L}^{-1} \text{NH}_4\text{F}$ solution was added. Then, 0.2 mL of $50 \text{ mg mL}^{-1} \text{Ca(II)}$ was added resulting in intense precipitation of CaF_2 in acidic solution. The contents were allowed to precipitate a few minutes and then centrifuged for 30 min at 12,000 rpm by Eppendorf micro-centrifuge (Model 5415D). The supernatant in each tube was decanted rapidly to another 2-mL micro-centrifuge tube for a second co-precipitation by adding NH_4F and Ca(II) as described above. At the conclusion of the second centrifugation, the liquid phase in each tube was collected and diluted to 30 mL with 1% v/v H_2SO_4 yielding 2% m/v $\text{K}_3\text{Mn}(\text{CN})_6$ in 1% v/v H_2SO_4 . This solution was stable for at least 48 h after preparation. Solution-based ICP-MS analysis of the diluted solutions of cleaned $\text{K}_3\text{Mn}(\text{CN})_6$ indicated that Pb impurity was reduced to below $0.02 \mu\text{g L}^{-1}$.

2.4. Samples and preparation

The accuracy of the procedure was verified by determination of Pb concentration in different certified reference materials (CRM)s, such as Nearshore seawater (CASS-4), Mussel tissue (SRM 2976) and Bone ash (SRM 1400). Coastal seawater samples were also analyzed by the procedure. CASS-4 was obtained from the National Research Council Canada, Ottawa, ON. The coastal seawater samples were collected at about 1 m depth from Galveston Bay, Galveston, TX into acid-cleaned polypropylene bottles and acidified to 0.1% (v/v) HNO_3 at the sampling site. At the laboratory, they were filtered through $0.45 \mu\text{m}$ membrane filters and stored in 0.1% v/v HNO_3 until analysis. Sub-samples (5.0 mL) of CASS-4 and coastal seawater were taken and acidified to 1% v/v HCl for analysis. Another set of sub-samples were spiked with 0.02 and $0.5 \mu\text{g L}^{-1}$ Pb for CASS-4 and coastal seawater, respectively, and analyzed simultaneously.

Bone ash (SRM 1400) was obtained from the National Institutes of Standards and Technology, Gaithersburg, MD. It is produced from high temperature calcinations of bone and thus is predominantly calcium phosphate matrix with $\mu\text{g g}^{-1}$ levels of levels of Al, F,

Fe, Sr and Zn. Sub-samples of about 25 mg were dissolved in 1.0 mL concentrated HNO₃ in 4-mL PTFE tubes (Savillex) at 120 °C using Digiprep Cube digestion system (SCP Science, Champlain, NY) as described elsewhere [17,33]. The solutions were heated to dryness. The final residue was dissolved and diluted to 10 mL with 1% v/v HNO₃. For HG-ICP-MS determination, 1.0 mL was taken and diluted to 20 mL with 1% v/v HCl.

Mussel tissue (SRM 2976) was also obtained from the National Institutes of Standards and Technology, Gaithersburg, MD. This material was characterized with As, Cu, Fe and Zn at high $\mu\text{g g}^{-1}$ levels. Approximately, 50 mg sub-samples were digested with 2.0 mL concentrated HNO₃ and 1.0 mL H₂O₂ in 60-mL screw-capped PTFE tubes (Savillex) at 140 °C for 2 h. At the conclusion, caps were opened and additional 1.0 mL H₂O₂ was added to hot solution to oxidize the organics. The contents were heated to dryness, and then redissolved with 2 mL water and heated again to remove all residual H₂O₂. The contents were then dissolved in 1% v/v HNO₃ and completed to 10 mL. Determinations were made in 10-fold diluted solutions in 1% v/v HCl.

2.5. Examining the stability K₃Mn(CN)₆

Preliminary experiments showed that potassium hexacyanomanganate(III), (K₃Mn(CN)₆), was highly unstable in water. Contact with water yielded insoluble black precipitate due to the formation of oxide or hydroxides. On the other hand, it dissolved readily and was stable to some extent in dilute acids, such as HCl and H₂SO₄. Therefore, 0.5% m/v K₃Mn(CN)₆ was prepared from reagent grade chemical directly (e.g., without any cleaning) in 1% v/v HCl, 1% v/v HNO₃ and 1% v/v H₂SO₄ to determine its stability in each acid solution. In this experiment, measurements were made with freshly prepared and aged K₃Mn(CN)₆ solution for 10 $\mu\text{g L}^{-1}$ Pb solutions acidified from 0 to 7% v/v HCl. Each Pb solution was mixed on-line with 0.5% m/v K₃Mn(CN)₆ solution and then reacted with 1% m/v NaBH₄.

2.6. Optimization of hydride generation conditions

Once the optimum medium for stabilization of K₃Mn(CN)₆ was identified, the effect of solution acidity was examined for 1.0 $\mu\text{g L}^{-1}$ Pb solutions prepared in HCl and H₂SO₄. The acidity was varied from 0 to 7% v/v for each acid. In this experiment, 0.5% m/v K₃Mn(CN)₆ solutions were prepared in 1% v/v H₂SO₄ from the cleaned stock solution (2% m/v) and mixed on-line similarly with the acidified sample solution.

The concentration of K₃Mn(CN)₆ solution was examined between 0 and 2.5% m/v K₃Mn(CN)₆ in 1% v/v H₂SO₄. The length of reaction coil (1.14 mm i.d. tygon tubing) was varied from 2 to 20 cm to affect the signals. Then, the flow rates for the sample and the nebulizer argon gas were optimized. The former was examined between 0.5 and 2.0 mL min⁻¹ and the latter was varied from 0.8 to 1.4 L min⁻¹. The sodium borohydride concentration was optimized by varying its concentration from 0 to 3% m/v for the highest Pb signals. The flow rates for K₃Mn(CN)₆ and NaBH₄ solutions were not varied and kept at 0.5 mL min⁻¹ and 1.0 mL min⁻¹, respectively, since all other variables were optimized for these settings.

2.7. Examination of matrix effects

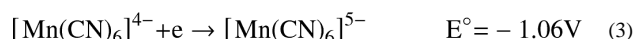
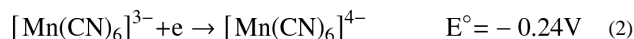
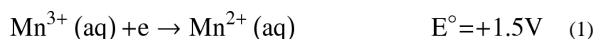
As for most hydride forming elements, determination of Pb by hydride generation is vulnerable to the interferences of transition metals (Co, Cu and Ni). In general, effects are manifested by depression or enhancement of the signals depending on the nature of acid-oxidant system and catalytic properties of the interfering element. Thus, the effects of a number of matrix elements, including As(III), Bi(III), Cd(II), Co(II), Cu(II), Fe(III), Mn(II), Ni(II), Sb(III), Se(IV), Sn(II) and Zn(II) were investigated for 1.0 $\mu\text{g L}^{-1}$ Pb(II) in the

presence of 0.1 and 0.5 $\mu\text{g mL}^{-1}$ of each element. Effects for Ca(II), K(I), Mg(II), and Na(I) were tested for 1000 $\mu\text{g mL}^{-1}$ solutions containing 1.0 $\mu\text{g L}^{-1}$ Pb(II).

3. Results and discussion

3.1. Stability of $\text{K}_3\text{Mn}(\text{CN})_6$ solution

Manganese forms a number of complexes with cyanide. The standard reduction potentials of hexacyanomanganate complexes are given below [37].

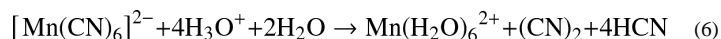


The data show that cyanide complexes of Mn(II) and Mn(I), $[\text{Mn}(\text{CN})_6]^{4-}$ and $[\text{Mn}(\text{CN})_6]^{5-}$, respectively, are stabilized best at Mn(III) oxidation state. In other words, both $[\text{Mn}(\text{CN})_6]^{5-}$ and $[\text{Mn}(\text{CN})_6]^{4-}$ ions are easily oxidized to $[\text{Mn}(\text{CN})_6]^{3-}$. The reduction of potential for $\text{Mn}^{3+} = \text{Mn}^{2+}$ system is +1.5 V which is relatively high in comparison to -0.24 V for $[\text{Mn}(\text{CN})_6]^{3-} = [\text{Mn}(\text{CN})_6]^{4-}$. This information also substantiates that Mn(III) is stabilized significantly by complexing with cyanide.

Despite its stability, hexacyanomanganate(III) hydrolyzes in water as shown in the reaction (4) yielding insoluble $\text{Mn}(\text{OH})_3$ [37].



The value of $K_{\text{diss}}/K_{\text{sp}}$ (e.g., the ratio of dissociation constant to the solubility product constant of $\text{Mn}(\text{OH})_3$) was estimated to be 2×10^4 , indicating that $[\text{Mn}(\text{CN})_6]^{3-}$ is thermodynamically unstable in water [37]. In acidic solution, however, $[\text{Mn}(\text{CN})_6]^{3-}$ undergoes disproportionation and decomposition reactions producing hexacyanomanganate(IV), $[\text{Mn}(\text{CN})_6]^{2-}$, as shown in reactions (5) and (6) [38].



It was reported that the disproportionation reaction (5) was very fast and quantitative at room temperature [38] yielding $[\text{Mn}(\text{CN})_6]^{2-}$ ion. Although this complex is more stable in acidic medium, it was also found to slowly decompose producing Mn(II) (e.g., $\text{Mn}(\text{H}_2\text{O})_6^{2+}$) and cyanogen gas, $(\text{CN})_2$ according to the reaction (6) [38].

3.2. Effects of acids on stability of $\text{K}_3\text{Mn}(\text{CN})_6$

The evidence from the literature [37, 38] clearly indicated that it would not be feasible to utilize $\text{K}_3\text{Mn}(\text{CN})_6$ robustly in generation of PbH_4 for quantitative determination of Pb unless the reagent is stabilized sufficiently. In initial attempts of PbH_4 generation, about 0.5% m/v $\text{K}_3\text{Mn}(\text{CN})_6$ was prepared in very dilute solutions of HCl, such as 0.2% and 0.5%

v/v HCl since Pb standard solutions were also prepared in the same acid. Evidently, it was feasible to prepare $K_3Mn(CN)_6$ solutions that enhanced the signals. However, temporal stability was poor. Visible precipitation or deposition was noted within an hour of preparation in some solutions, especially with lower acid concentration. This result was consistent with the literature and was indicative of the slow degradation of the reagent in dilute acid solutions. To overcome this hurdle, additional experiments were performed by increasing HCl concentration as well as affecting the stability with dilute solutions of HNO_3 and H_2SO_4 . The results of the experiments are illustrated in Fig. 2 for 1% v/v solutions of HCl, HNO_3 and H_2SO_4 . Signals for $10 \mu g L^{-1}$ Pb solutions were almost identical when measurements were made with freshly prepared $K_3Mn(CN)_6$ solutions regardless of the acid used for dissolution. On the other hand, extended or long-term stability of the reagent varied remarkably depending on the acid. Apparently, neither 1% v/v HCl nor 1% v/v HNO_3 medium provided adequate stabilization (Fig. 2A and 2B). For $K_3Mn(CN)_6$ solution prepared in 1% v/v HCl, signals decreased significantly to about 52% of the initial signals (e.g., 48% lower) when measurements were repeated 6 h later (see Fig. 2A). According to the reactions 5 and 6, this decrease was due to the instability of the acid dissolution product, *viz.* $[Mn(CN)_6]^{2-}$ in 1% v/v HCl. Higher concentrations of HCl (e.g., 5% v/v) provided better stability. Yet, signals did drop by 30 to 35% within 6 h. Degradation of $K_3Mn(CN)_6$ in 1% v/v HNO_3 was even faster such that 3 h later the sensitivity dropped by 72% in comparison to that for the fresh solution (Fig. 2B). This was attributed to the oxidizing nature of HNO_3 , *viz.* decomposition of $[Mn(CN)_6]^{2-}$ to Mn(IV). Further, a brown-black precipitate formed as the solution was allowed to wait longer. This precipitate was thought to be manganese(IV) oxide as a result of decomposition of $[Mn(CN)_6]^{2-}$ in HNO_3 medium.

Unlike those in HCl and HNO_3 , $K_3Mn(CN)_6$ was found to be stable in 1% v/v H_2SO_4 medium (Fig. 2C). The signals for $10 \mu g L^{-1}$ Pb solutions were almost identical for fresh and aged solutions of 0.5% m/v $K_3Mn(CN)_6$. No significant changes occurred in signals when measurements were performed 24 h later with the same $K_3Mn(CN)_6$ solution. Sensitivity varied only about 3 to 5%. Stability was not examined instrumentally beyond 24-h period. However, no significant degradation or precipitation was noted for at least 48 h when $K_3Mn(CN)_6$ solutions were inspected visually.

Higher concentrations of H_2SO_4 (ca. 5 to 6% v/v) did not deteriorate its stability, instead facilitated the dissolution of the reagent, which was advantageous for preparing concentrated stock solutions. Saturation data for $K_3Mn(CN)_6$ in dilute H_2SO_4 is not available; however, our results suggested that up to 8% m/v solutions could be prepared in 2 to 3% v/v H_2SO_4 . Consequently, experimental solutions of $K_3Mn(CN)_6$ were prepared in dilute H_2SO_4 and cleaned according to the procedure described in section 2.3 in subsequent experiments.

3.3. Optimization of solution acidity for generation of plumbane

Hydrochloric acid is often the desired reagent for acidification of solutions for generation of plumbane (PbH_4) in the presence of potassium hexacyanoferrate(III), $K_3Fe(CN)_6$ [12–17, 27–33]. In this study, however, $K_3Mn(CN)_6$ was best stabilized in dilute H_2SO_4 , therefore, we attempted to examine the performances of HCl and H_2SO_4 on generation of plumbane within a concentration gradient of 0 to 7% v/v. The results are illustrated in Fig. 3. The optimum acidity was between 0.5 to 2% v/v for HCl, which was consistent with that in Fig. 2C. Unlike that for HCl, the optimum range for H_2SO_4 was significantly narrow (0 to 0.5% v/v) exhibiting an optimum concentration around 0.25% v/v H_2SO_4 . The sensitivity was relatively better (e.g., 15 to 20%) in H_2SO_4 medium. Nevertheless, HCl appeared to be more robust because of the broader working range of sample acidity. Thus, all solutions in subsequent studies were prepared in 1% v/v HCl and mixed on-line with $K_3Mn(CN)_6$ solutions in 1% v/v H_2SO_4 .

3.4. Effect of $K_3Mn(CN)_6$ concentration on PbH_4 generation

The effect of $K_3Mn(CN)_6$ concentration on generation of PbH_4 was studied between 0.1 and 2.5% m/v levels. Signals for $1.0 \mu\text{g L}^{-1}$ Pb solutions increased steeply with 0.1% m/v $K_3Mn(CN)_6$ indicating that very small concentration of $K_3Mn(CN)_6$ was sufficient for the formation of PbH_4 from acidic solutions. This pattern was consistent with that for $K_3Fe(CN)_6$ that also boosted Pb signals at relatively small levels [12,17,31]. Optimum concentration was around 0.5% m/v $K_3Mn(CN)_6$ to attain maximum signals. However, it should be noted that this concentration reflects the performance of $K_3Mn(CN)_6$ in the absence of matrix or any interferences. Further, Pb is a highly ubiquitous element. Consequently, its determination suffers from contamination from the reagents that hampers the limit of detection (LOD), especially when utilizing highly sensitive approaches, such as hydride generation. Thus, the concentration of $K_3Mn(CN)_6$ was tentatively kept at 0.5% m/v until further examination under matrix conditions.

The generation of PbH_4 is often assumed to take place via oxidation of Pb(II) to Pb(IV) with the aid of the additives in acidic solution. The enhancement in the case of $K_3Mn(CN)_6$, however, cannot be attributed to the oxidation of Pb^{2+} to Pb^{4+} since hexacyanomanganate(III) ($[Mn(CN)_6]^{3-}$) is oxidized to hexacyanomanganate(IV) ($[Mn(CN)_6]^{2-}$) in dilute H_2SO_4 solution as mentioned above [37, 38], *viz.* reduction of $[Mn(CN)_6]^{2-}$ to $[Mn(CN)_6]^{3-}$ is not favored. It is therefore likely that $K_3Mn(CN)_6$, albeit $[Mn(CN)_6]^{2-}$ complex, affected the formation of PbH_4 by the same mechanism involving the formation of reactive hydroborane intermediates facilitating the generation of PbH_4 as proposed in the presence of $K_3Fe(CN)_6$ in that the generation of PbH_4 was found to be independent of the sequence whether or not $K_3Fe(CN)_6$ was mixed with acidic sample solution or $NaBH_4$ solution first [31]. This phenomenon was ascribed to the formation of reactive “borane complex intermediates” in the presence of $K_3Fe(CN)_6$ affecting the generation of PbH_4 from Pb(II).

3.5. Optimization of $NaBH_4$ concentration and flow rates

The influence of $NaBH_4$ concentration on signals is shown in Fig. 4A for Pb ($1.0 \mu\text{g L}^{-1}$) and 0.5% m/v $K_3Mn(CN)_6$ setup. $NaBH_4$ was highly influential on the generation of plumbane. In comparison to those with 1% m/v $NaBH_4$, the signals constantly increased up to 1.5% m/v and exhibited a plateau with further increase up to 3% m/v. Apparently, a concentration of 2% m/v was optimum to maintain the sensitivity. This result was also consistent with previous results reported for generation of PbH_4 [17]. Water vapor is a major by-product of the reaction of $NaBH_4$ with HCl, which could induce instability in plasma at higher concentrations of $NaBH_4$ as reported elsewhere [17]. No significant instability was noted in this study from continuous introduction of 2% m/v $NaBH_4$ since the cooled-spray chamber (2°C) afforded efficient removal of water vapor before reaching to plasma.

The effect of the nebulizer flow rate on signals is shown in Fig. 4B. The sensitivity was at maximum between 1.1 and 1.2 L min^{-1} when the flow rate of nebulizer argon was varied from 0.8 to 1.4 L min^{-1} . Signals dropped significantly at lower and higher flow rates due to the alterations in the sampling depth in the plasma. The flow rate for the sample solution was around 1.0 mL min^{-1} to achieve adequate sensitivity (Fig. 4C). Signals increased with increasing flow rates up to 1.5 to 2.0 mL min^{-1} , but at the cost of increased sample consumption. Thus, the flow rate of the sample solution was kept constant at 1.0 mL min^{-1} .

3.6. Analytical figures of merit

The detection limits obtained for 1% v/v HCl blanks with 2% m/v $K_3Mn(CN)_6$ were 0.007, 0.007 and $0.008 \mu\text{g L}^{-1}$ for ^{206}Pb , ^{207}Pb and ^{208}Pb isotopes. These detection limits reflect the analyte concentration equivalent to three times the standard deviation of the blanks

signals ($n=13$). Calibration curves were linear within 0.02 to 5.0 $\mu\text{g L}^{-1}$ ($r^2 = 0.998 - 1.0$). The detection limits for traditional ICP-MS measurements were 0.078, 0.075 and 0.090 $\mu\text{g L}^{-1}$ for ^{206}Pb , ^{207}Pb and ^{208}Pb isotopes, respectively. In comparison to the traditional ICP-MS, the sensitivity was enhanced by a factor of 42 to 48 based on the slopes of the calibration curves for direct ICP-MS and HG-ICP-MS. However, the enhancement in the detection limits were about 10-fold because of the higher background signals at HG mode. The average signal-to-ratio (S/N) at 1.0 $\mu\text{g L}^{-1}$ was, however, about 18 to 20 which was mainly because of the residual Pb impurities in $\text{K}_3\text{Mn}(\text{CN})_6$ solution despite efficient cleaning by coprecipitation. Relative standard deviations (RSD) varied between 0.4% and 6.3% for replicate measurements ($n = 6$) of the standard solutions (0.02 to 2 $\mu\text{g L}^{-1}$). No memory effects were noted for replicate measurements even with 10 $\mu\text{g L}^{-1}$ Pb solution that was continuously introduced during method optimization. A washout of 20 s with 1% v/v HCl (at 4 mL min^{-1}) was sufficient for cleaning up the system between samples.

3.7. Tolerance to chemical interferences

Hydride generation (HG) offers the capability to alleviate the matrix interferences and better sensitivity for accurate determination by ICP-MS. Nevertheless, the chemical interferences from transition metals are still important setbacks in HG approaches [1,2,4,15,16,26]. The interferences in solution are mainly mediated by the transition metals, while the hydride forming elements cause interferences in vapor phase. Further, the interfering elements vary greatly with the hydride generation medium. Wang et al. [18], for instance, reported depressive effects from Cu(II), Fe(III), Mn(II) and Ni(II) on plumbane generation in HCl-H₂O₂ medium, while the same elements as well as Co(II) and Zn(II) enhanced the signals in HNO₃-H₂O₂ medium [39,40]. In contrast, Co(II) induced interferences in determination of Pb by hydride generation in $\text{K}_3\text{Fe}(\text{CN})_6$ medium [33]. The depressive effect was attributed to the reduction of Fe(III) and Pb(II) through cobalt borides. Among the transition metals, Cu(II) has been the most reported for its interferences in the presence of oxidizing agents, such as hexacyanoferrate(III) [17], hydrogen peroxide [18] and cerium(IV) ammonium nitrate [26].

The tolerance of $\text{K}_3\text{Mn}(\text{CN})_6$ to the effects of alkali, alkaline and transition metals and hydride forming elements are summarized in Table 2. The values reflect the relative responses obtained from 1.0 $\mu\text{g L}^{-1}$ Pb solution with 500 $\mu\text{g L}^{-1}$ of the interfering element to that of single element Pb solution using 0.5% m/v $\text{K}_3\text{Mn}(\text{CN})_6$. No significant interferences were observed from any of the transition metals and hydride forming elements, excluding Cu(II), when test concentration was varied from 100 to 500 $\mu\text{g L}^{-1}$. Signals varied from 94% for Ni(II) to 106% for Zn(II). The test concentrations for the alkali (Na and K) and alkaline earth elements (Ca and Mg) were 1000 $\mu\text{g mL}^{-1}$. The relative responses in the solutions of these elements varied between 98% (Mg) and 106% (K), indicating that they were highly benign in the generation of PbH_4 .

Catalytic decomposition of $[\text{Fe}(\text{CN})_6]^{3-}$ was reported in the presence Cu(II) [41,42]. In this study, Cu(II) induced severe depression in $\text{K}_3\text{Mn}(\text{CN})_6$ medium, suggesting that interferences of Cu(II) were due to the decomposition of $[\text{Mn}(\text{CN})_6]^{3-}$ (e.g., $[\text{Mn}(\text{CN})_6]^{2-}$). The instability of the reagent could have also contributed to the severity of the interferences such that the signals were suppressed by more than 50% even in the presence of 0.1 $\mu\text{g mL}^{-1}$ Cu(II). To overcome this hurdle, the concentration of $\text{K}_3\text{Mn}(\text{CN})_6$ was re-examined along different Cu(II) concentrations. The results are shown in Fig. 5 for 0.5, 1 and 2% m/v $\text{K}_3\text{Mn}(\text{CN})_6$. It is clear that 0.5% m/v $\text{K}_3\text{Mn}(\text{CN})_6$ was not adequate to abate the depressive effects of Cu(II), though it performed successfully in the presence of other interfering elements, such as Ni(II) and Co(II). The signals, however, improved significantly by increasing $\text{K}_3\text{Mn}(\text{CN})_6$ concentration to 2% m/v for which percent relative response was about 92% in the presence of 0.1 $\mu\text{g mL}^{-1}$ Cu(II) matrix.

Table 3 summarizes the performance of the method in the presence of 2% m/v $K_3Mn(CN)_6$ with those reported earlier. It is clear that Cu(II) was the only single element that interfered with the formation of PbH_4 in any medium, even in the presence of potassium hexacyanoferrate(III) medium [15,17,43]. The effects were severest in both $HNO_3-H_2O_2$ [16] and $HCl-H_2O_2$ [16, 18] such that accuracy was low even in freshwater samples containing part per billion levels of transition metal ions [16]. In $HNO_3-H_2O_2$, isotope dilution (ID) approach provided better detection limits and accuracy [16]. The detection limits obtained by using oxalic acid-ammonium cerium(IV) nitrate were similar to those in this study, but $(NH_4)_2Ce(NO_3)_6$ medium appears to be highly susceptible to the depressive effects of Cu(II) despite the masking ability of oxalate ion [26].

3.7. Application to real samples

Calibration was made with single element external standards for the analysis of samples by the optimized HG-ICP-MS procedure. The standard solutions ranged from 0, 0.02, 0.05, 0.1, 0.2, 0.5, 1.0 to 2.0 $\mu g L^{-1}$ Pb in 1% v/v HCl. The signals from five standard solutions bracketing that of the sample were used to calculate the Pb concentration in the samples. The Nearshore certified reference seawater (CASS-4) and the coastal seawater were analyzed by adjusting the acidity of sub-samples to 1% v/v HCl. Because the certified value of Pb in CASS-4 was within the vicinity of the detection limits of the method, accuracy was further verified with spiked solutions for both water samples. The results are summarized in Table 4 for ^{208}Pb isotope. The experimental results for CASS-4 were consistent with the certified value of Pb in CASS-4 at 95% confidence level. The concentration of Pb in the coastal seawater was much higher which was attributed to the contributions from local sources (creeks and rivers) as well as leaching from the surface and bottom sediments. Similarly, the concentrations obtained from the unspiked samples were consistent with that for the spiked seawater samples. The concentration of Cu(II) in CASS-4 was $0.592 \pm 0.055 \mu g L^{-1}$ and $0.920 \pm 0.06 \mu g L^{-1}$ in coastal seawater. These levels were well below the threshold value of Cu(II) ($100 \mu g L^{-1}$) to affect the accuracy.

The results for Bone ash (SRM 1400) and Mussel tissue (SRM 2976) are also summarized in Table 4. The bone ash samples were rich in calcium and phosphate along with aluminum, iron, fluoride and magnesium at $\mu g mL^{-1}$ levels. The mussel tissue (SRM 2976) was composed of organic matrix with high levels of Fe and Zn. Determinations were performed in 20- and 10-fold diluted solutions for SRM 1400 and SRM 2976, respectively, to bring the concentration of Pb within the calibration range. Accurate results were obtained for Pb in both reference materials. The experimental concentrations were in agreement with the certified values within 95% confidence level (Table 4).

4. Conclusions

Efficiency of potassium hexacyanoferrate(III) for generation of lead hydride has been known for decades now. In this study, we have utilized another transition metal cyanide complex, potassium hexacyanomanganate(III), for the first time for generation of plumbane and investigated its performance in determination of Pb by HG-ICP-MS. Potassium hexacyanomanganate(III) is very insoluble and unstable in water that renders this catalytically active reagent unusable for hydride generation. On the other hand, the acidic conditions provided by H_2SO_4 were conducive to achieve better stabilization. The results confirmed that $K_3Mn(CN)_6$ was uniquely suited for effective generation of plumbane from acidic sample solutions of Pb(II) when interacted with $NaBH_4$. It is assumed that that hexacyanomanganate(III) mediates the generation of PbH_4 by similar mechanism as hexacyanoferrate(III) does. Future studies are expected to shed light onto the mechanism of this process.

The method described here is highly sensitive and robust for quantitative determination of Pb accurately in various samples by ICP-MS and other atomic spectroscopy techniques. It is also not affected from the presence of common transition metals (Co, Cr, Fe, Ni,) and hydride forming elements. Cu(II) impacts the stability and hence performance of $K_3Mn(CN)_6$ adversely at sub-ppm levels. Nevertheless, the effects could easily be abated using on-line approach and higher concentrations of $K_3Mn(CN)_6$. Because of the simplicity, the method could easily be interfaced to inductively coupled plasma atomic emission spectroscopy (ICP-AES) for sub-ppb determination of Pb. It is envisioned that this catalytically active reagent could also offer the capability of hydride generation for multiple element determination.

Acknowledgments

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Highlights

- Potassium hexacyanomanganate(III), $(K_3Mn(CN)_6)$, was utilized first time for hydride generation (HG).
- Hexacyanomanganate(III) promoted generation of lead hydride (PbH_4) remarkably.
- The HG method using $K_3Mn(CN)_6$ enhanced sensitivity by at least 40-fold.
- The method detection limits for Pb were as low as 7 ng L^{-1} by ICP-MS.
- The method is highly suitable for quantitative determination of Pb in various samples and salt matrices by ICP-MS.

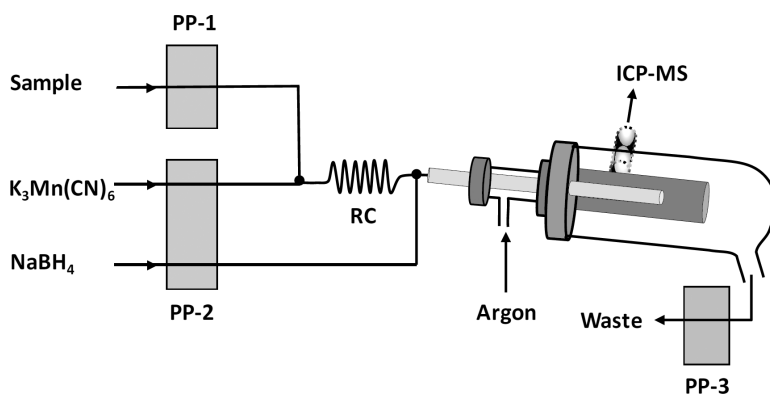


Fig. 1. Schematic illustration of the hydride generation manifold. The gas–liquid separator is the stand–alone glass double pass spray chamber with 100 mL inner volume. The spray chamber is peltier cooled to 2 °C for removal excess water vapor. Reaction coil (RC) is 5.0 cm long tygon tubing (1.14 mm i.d.).

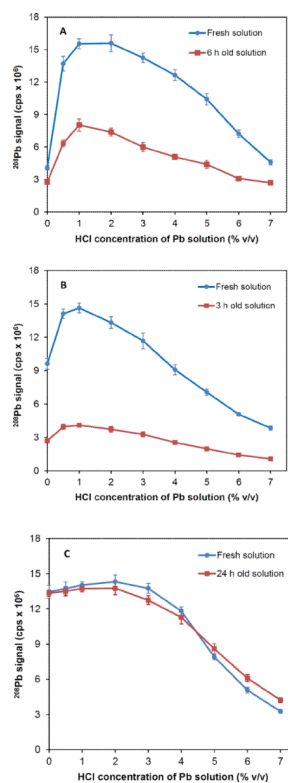


Fig. 2. Temporal stability of 0.5% m/v $K_3Mn(CN)_6$ solutions prepared in (A) 1% v/v HCl, (B) 1% v/v HNO_3 , (C) 1% v/v H_2SO_4 . Signals were collected for $10 \mu g L^{-1}$ Pb solution acidified from 0 to 7% v/v HCl.

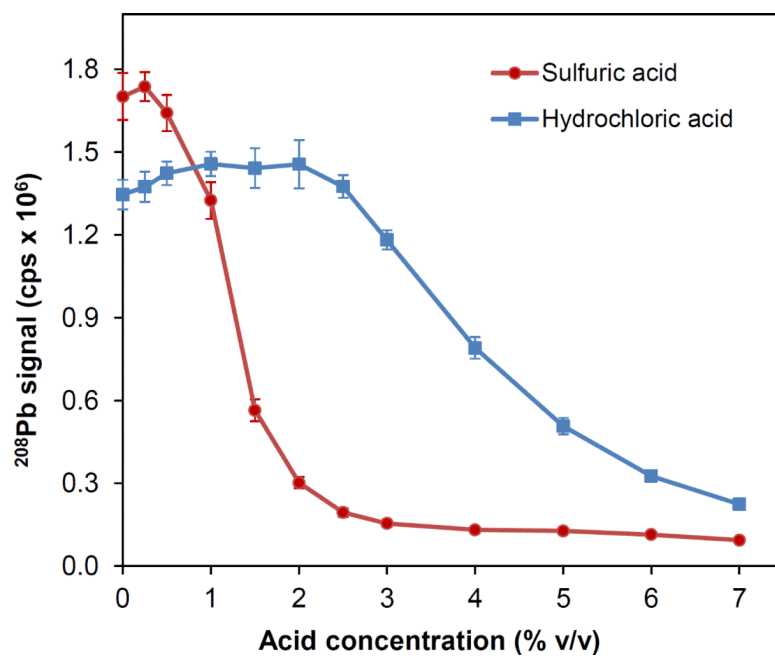


Fig. 3. Effect of solution acidity adjusted by HCl or H_2SO_4 on the signals profiles for $1.0 \mu\text{g L}^{-1}$ Pb. $\text{K}_3\text{Mn}(\text{CN})_6 = 0.5\%$ m/v in 1% v/v H_2SO_4 , $\text{NaBH}_4 = 1\%$ m/v in 0.1% m/v NaOH.

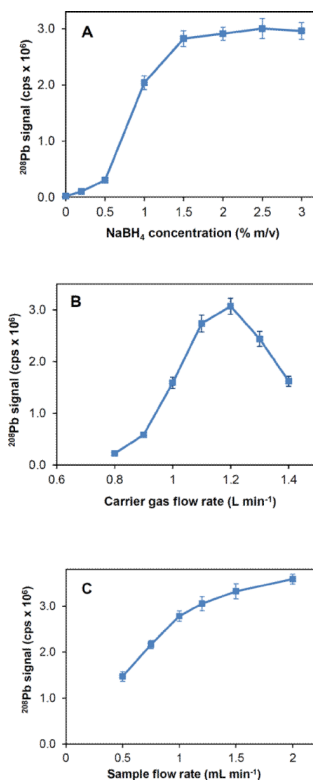


Fig. 4. Effects of various experimental parameters on signals during generation of PbH_4 in $1.0 \mu\text{g L}^{-1}$ Pb using 0.5% m/v $\text{K}_3\text{Mn}(\text{CN})_6$. (A) NaBH_4 concentration, (B) Carrier (nebulizer) argon flow rate, and (C) flow rate of sample solution.

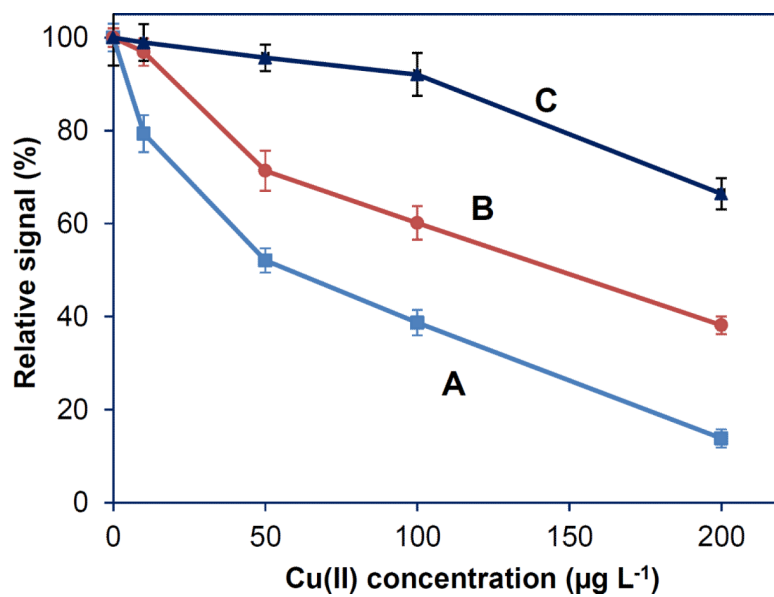


Fig. 5. The effect of Cu(II) concentration on signals for $1.0 \mu\text{g L}^{-1}$ Pb solution as a function of $\text{K}_3\text{Mn}(\text{CN})_6$ concentration. (A) 0.5% m/v $\text{K}_3\text{Mn}(\text{CN})_6$, (B) 1.0% m/v $\text{K}_3\text{Mn}(\text{CN})_6$, (C) 2% m/v $\text{K}_3\text{Mn}(\text{CN})_6$.

Table 1

Operating conditions for Varian 820MS ICP–MS instrument and hydride generation system

<i>ICP-MS</i>	
RF Power (kW)	1.4
Plasma Ar flow (L min ⁻¹)	18
Auxiliary Ar flow (L min ⁻¹)	1.8
Nebulizer Ar flow (L min ⁻¹)	1.2
Sheath Ar flow (L min ⁻¹)	0.1
Sampling depth (mm)	7
Pump rate (mL min ⁻¹)	1.0
Stabilization time (sec)	40
Spray chamber temperature (°C)	2
Scan mode	Peak hopping
Dwell time (ms)	50
Points/peak	1
Scans/peak	6
Scans/replicate	10
Isotopes measured	²⁰⁶ Pb, ²⁰⁷ Pb and ²⁰⁸ Pb

<i>Hydride generation</i>	
Sample acidity – flow rate	1% v/v HCl – 1.0 mL min ⁻¹
K ₃ Mn(CN) ₆ concentration – flow rate	2% m/v – 0.5 mL min ⁻¹
NaBH ₄ concentration – flow rate	2% m/v – 1.0 mL min ⁻¹

Table 2Effects of matrix elements on relative signals in $1.0 \mu\text{g L}^{-1}$ Pb solution using 0.5% m/v $\text{K}_3\text{Mn}(\text{CN})_6$

Element	Concentration ($\mu\text{g L}^{-1}$)	Relative signal (%)
As(III)	500	96 ± 2
Bi(III)	500	102 ± 2
Co(II)	500	98 ± 5
Cr(III)	500	102 ± 5
Cu(II)	100	42 ± 3
	500	12 ± 2
Fe(III)	500	103 ± 2
Mn(II)	500	98 ± 4
Ni(II)	500	94 ± 7
Sb(III)	500	100 ± 2
Se(IV)	500	98 ± 3
Sn(II)	500	99 ± 2
Zn(II)	500	106 ± 4

Table 3
Comparison of the performance of the procedure with other methods applied to the determination of Pb by hydride generation

Technique	Medium	Matrix	Concentration ($\mu\text{g mL}^{-1}$)	R(%)	LOD ($\mu\text{g L}^{-1}$)	Ref.#
	HCl					This work
HG-ICPMS	$\text{K}_3\text{Mn}(\text{CN})_6$	Cu(II)	0.1	92	0.008	
		Cu(II)	0.5	90		
HG-ICPMS	$\text{HCl-H}_2\text{C}_2\text{O}_4$	Co(II)	0.5	91	0.003	15
	$\text{K}_3\text{Fe}(\text{CN})_6$	Ni(II)	0.5	91		
	Freshwater ^s			130		
HG-ICPMS	$\text{HNO}_3\text{-H}_2\text{O}_2$	Seawater	–	89	0.2	16
		20% NaCl		41		
	Freshwater ^a			100		
HG-ID-ICPMS	$\text{HNO}_3\text{-H}_2\text{O}_2$	Seawater	–	99	0.02	16
		20% NaCl		102		
	HCl					
HG-ICPAES	$\text{K}_3\text{Fe}(\text{CN})_6$	Cu(II)	1.0	72	0.1	17
		Cu(II)	0.1	36		
FI-HG-ICPMS	$\text{HCl-H}_2\text{O}_2$	Fe(III)	0.1	41	0.04	18
		Ni(II)	0.5	93		
	$\text{H}_2\text{C}_2\text{O}_4$		0.02	99	0.007	26
HG-ETV-ICPMS	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	Cu(II)	0.1	64		
	HCl					
HG-ETV-ICPMS	$\text{K}_3\text{Fe}(\text{CN})_6$	Lakewater ^b	–	98	0.07	32
	HCl					
HG-ICPAES	HCl	Cu(II)	1.0	50		43
	$\text{K}_3\text{Fe}(\text{CN})_6$	Fe(III)	1.0	92	0.7	

^aSRM 1623, NIST Freshwater certified reference material.

^bNWRI TM-28.3 certified reference material (trace elements fortified water from Lake Ontario), (5-fold diluted).

Table 4

Elemental concentrations for ^{208}Pb from the analysis of Nearshore certified seawater reference material (CASS-4), coastal seawater, bone ash (SRM 1400) and mussel tissue (SRM 2976) certified reference materials by HG-ICP-MS procedure. Results are given as mean \pm standard deviation of five replicate analyses for each sample. Spike concentrations are 0.02 and 0.05 $\mu\text{g L}^{-1}$ for CASS-4 and coastal seawater, respectively

Sample	Determined		Certified value
	Unspiked sample	Spiked sample	
Nearshore seawater (CASS-4)($\mu\text{g L}^{-1}$)	0.0013 \pm 0.004	0.030 \pm 0.006	0.0098 \pm 0.0036
Coastal seawater($\mu\text{g L}^{-1}$)	0.580 \pm 0.020	1.18 \pm 0.06	–
Bone ash (SRM 1400) ($\mu\text{g g}^{-1}$)	8.93 \pm 0.34	–	9.07 \pm 0.12
Mussel tissue (SRM 2976) ($\mu\text{g g}^{-1}$)	1.33 \pm 0.22	–	1.19 \pm 0.18