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Metal ion-assisted photochemical vapor generation for the determination of lead in environmental samples by MC-ICPMS

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ABSTRACT

A novel and sensitive approach for the accurate and precise determination of Pb in environmental samples is presented using transition metal ion-assisted photochemical vapor generation (PVG) for sample introduction with MC-ICPMS detection. A significant improvement in PVG efficiency of lead is achieved in the presence of transition metal ions (Co^{2+} and Ni^{2+}) in solutions of 5% (v/v) formic acid. The determination of Pb in digests of sediment or soil samples, is readily achieved because of coexisting transition metal ions which facilitate the PVG reaction. A method detection limit of 0.005 ng g^{-1} (3σ) was obtained for Pb using external calibration, comparable to that obtained using hydride generation (HG) ICPMS. However, PVG methodology is simpler, results in lower blanks and avoids unstable reagents. The accuracy of the proposed method was demonstrated by analysis of several environmental certified reference materials (SLRS-5 and SRM1640a river water CRMs, and MESS-3, MESS-4 and SRM2702 sediments) with satisfying results. High precision of determination (<0.4 % RSD) of Pb in river water and sediments was realized by isotope dilution quantification.

INTRODUCTION

Lead is a well-known environmental pollutant. Exposure through inhalation or ingestion can cause a number of adverse human health effects[1-4]. Children are more susceptible to Pb poisoning than adults; exposure to low concentrations can enhance the risk for detrimental neurological development of children.[3-7] Anthropogenic activities, such as mining, smelting, industrial uses, waste incineration and coal burning, have resulted in significant emissions of Pb into the environment. Although its release has been dramatically reduced after years of effort, adverse exposure to Pb continues to be a significant public health concern[6, 8-11]. Elucidation of the distribution and concentration in environmental samples is essential for continued monitoring/controlling of Pb contamination and assessment of exposure.

Atomic spectrometry based techniques comprise most popular methods for the determination of elements in environment samples with inductively coupled plasma mass spectrometry (ICPMS) being one of the most powerful providing low detection limits, wide linear range, and high sample throughput[12]. Analytical precision can be enhanced by use of multi-collector instrumentation (MC-ICPMS) with isotope dilution quantification[13]. Unfortunately, typical analytical performance with classical introduction based on sample solution nebulization introduction cannot address the direct determination of extremely low concentrations of Pb in environmental samples (e.g., low ppt in aquatic samples) or samples having a complex matrix[14, 15].

Chemical vapor generation (CVG) is an important sample introduction technique widely used in atomic spectrometry as it provides enhanced sensitivity and selectivity. Hydride generation (HG) using tetrahydroborate (III) (THB) remains the most widespread CVG technique for the determination of trace and ultratrace elements due to its high vapor generation efficiency and efficient matrix separation[16]. Generation of lead hydride for analytical purposes was first reported by Thompson and Thomerson in 1974[17]. However, plumbane (PH_4) generation is largely dependent on the experimental conditions and

generation efficiency is rather low in acid media through reaction with tetrahydroborate only. The presence of suitable oxidizing agents (together with transition ions or chelating agents) facilitates plumbane generation reactions, resulting in significant improvement in generation efficiency and resultant sensitivity for determination of Pb[18-22]. It is assumed that two steps are involved in this reaction: oxidation of Pb(II) to Pb(IV) followed by hydride transfer to form PbH_4. Although the mechanism of HG of Pb is still under dispute[18, 23], potassium hexacyanoferrate (III) ($K_3Fe(CN)_6$) is undoubtedly the most effective reagent used to enhance generation efficiency of plumbane from acidic solutions and thus is inevitably used for routine determination of Pb. Unfortunately, the high blank arising from $K_3[Fe(CN)_6]$ deteriorates the detection limit, making it difficult to determine trace/ultratrace concentrations of Pb in environmental samples.[24] Purification of $K_3[Fe(CN)_6]$ prior to use has been proposed as a means to minimize the blank [24, 25], but the cleaning procedure is complicated, labor intensive and time consuming. Furthermore, the instability of $KBH_4/NaBH_4$ reductant solutions and matrix interferences limit the widespread usage of HG for trace Pb determinations[26].

Photochemical vapor generation (PVG) is emerging as a powerful alternative to HG for sample introduction, utilizing free radicals generated by photo-redox reactions in the presence of low molecular weight organic compounds[27-29]. It not only retains the principle advantages of conventional CVG, but provides for simpler reactions and greener analytical chemistry. Currently, there are few reports of vapor generation of Pb, likely due to poor conversion efficiency[27, 30]. The purpose of this work was to develop a novel, sensitive, and green method for the accurate and precise determination of trace amounts of Pb in environmental samples using metal ion-assisted PVG coupled with MC-ICPMS detection. PVG efficiency is significantly enhanced by the presence of transition metals (such as Co^{2+} and Ni^{2+}) in a dilute formic acid medium. To date, this is the first report of use of transition metal ions enhancing PVG for the determination of trace Pb in environmental samples. PVG for Pb in sediment and soil digests is

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readily achieved because of the endogenous transition metal ions present in the sample matrix. The accuracy of the proposed method is demonstrated by successful analysis of several environmental certified reference materials

EXPERIMENTAL SECTION

Instrumentation. A Thermo Fisher Scientific (Bremen, Germany) Neptune MC-ICPMS equipped with nine Faraday cups and a combined cyclonic and Scott-type spray chamber was used for all measurements. The spray chamber has two inlets; one accommodating a 50 µL min^{-1} MCN50 PFA nebulizer (Elemental Scientific, Omaha, NE, USA) and a second for gaseous sample introduction. A plug-in quartz torch with a quartz injector and a Pt guard electrode were used. A schematic of the UV-PVG photoreactor interfaced to the MC-ICPMS is shown in Figure 1. The UV-PVG system consists of a unique 19 W photoreactor obtained from Beijing Titan Instruments Co. (Beijing, China). The sample solution was pumped through a narrow bore synthetic quartz tube (800 µL internal volume) internally positioned along the central axis of the low pressure mercury discharge. This allowed efficient and uniform irradiation of a thin film of the sample from all directions and with deep UV lines from the discharge. The photoreactor was enclosed in aluminium foil to protect the operator from exposure to the UV. Argon carrier gas was used at a flow rate of 0.33 L min^{-1} and introduced through a "Y" connection between the outlet of the photoreactor and a homemade gas liquid separator (GLS, ~ 2 mL internal volume) maintained at 0 °C by immersion in an ice bath to miminize any transport of liquid droplets derived from condensation of water vapor to the ICP. The generated analyte vapors were directed from the outlet of the GLS to the gas inlet port of the spray chamber *via* a 0.25 m length of Teflon lined Tygon tubing (0.25 in o.d., VWR International).
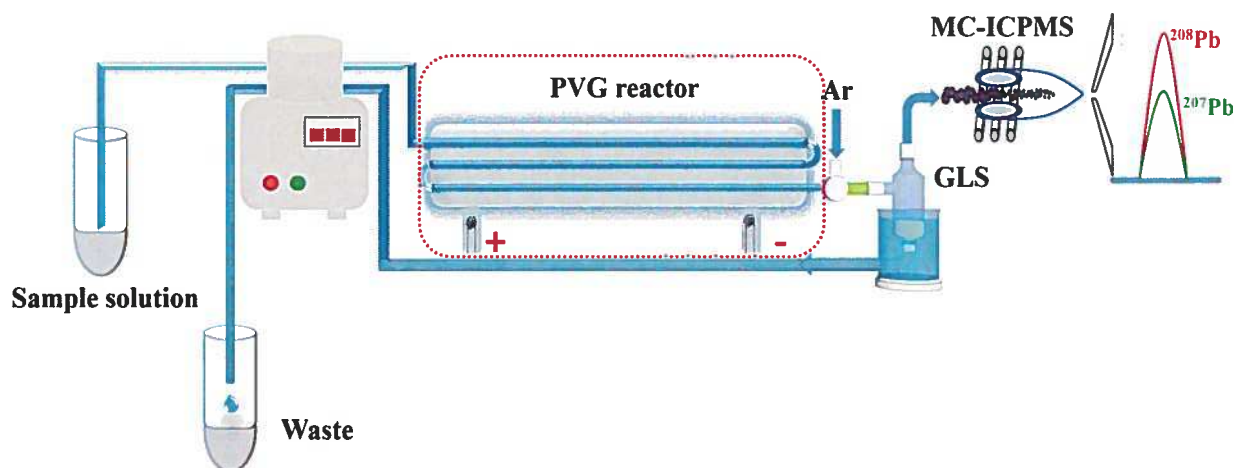
Figure 1. Schematic of the UV-PVG system interfaced to the MC-ICPMS.

A Perimax peristaltic pump (Spetec GmbH, Berghamer, Germany) was used to deliver sample solution at a flow rate of 1.2 mL min^{-1} to the photoreactor. A Multiwave 3000 microwave oven (PerkinElmer, Woodbridge, Ontario, Canada) was used for sample digestions.

Reagents and solutions. Nitric and hydrochloric acids were purified in-house prior to use by sub-boiling distillation of reagent grade feedstock in a quartz still. Environmental grade HF was purchased from Anachemia Science (Montreal, Quebec, Canada). High purity de-ionized water (DIW) was obtained from a NanoPure mixed bed ion exchange system fed with reverse osmosis domestic feed water (Barnstead/Thermolyne Corp, Iowa, USA). High purity formic (88%), and glacial acetic acids were obtained from GFS Chemicals Inc. (Powell, OH, USA). A 2 M BrCl solution was prepared in a fume hood by dissolution of 27 g of reagent grade KBr (Fisher Scientific, Ottawa, Canada) in 2.5 L of HCl in a glass container followed by slow addition of 38 g reagent grade $KBrO_3$(Fisher Scientific, Ottawa, Canada). A rinse solution containing 0.04 M BrCl was preparation by dilution of the 2 M BrCl with DIW.

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A natural abundance Pb stock solution of 3765.8 µg g^{-1} was prepared by dissolution of 0.4 g of the high purity metal (Johnson, Matthey & Co. Limited, London, UK) in 15 mL of 10% HNO$_3$ followed by dilution with DIW. Natural abundance stock solutions of Co, Ni and Fe of 1524.3 µg g^{-1}, 2542.9 µg g^{-1} and 1374.5 µg g^{-1}, respectively, were prepared by dissolution of their high purity metals in a few mLs of HNO$_3$ and HCl followed by dilution with DIW. Working standard solutions containing 10.18 and 0.4020 µg g^{-1} for Pb used for both the reverse spike isotope dilution of the enriched spike solutions and for standard additions calibration, respectively, were prepared by dilution of the stock with 2 % HNO$_3$ solution. Enriched ^{207}Pb isotope (as metal, 92%+), purchased from Trace Sciences International (Richmond Hill, Ontario, Canada) was dissolved in 10% HNO$_3$ and diluted with DIW. Working spike solutions of 5.0 and 0.070 µg g^{-1} were prepared by dilution of the ^{207}Pb stock solution with 2 % HNO$_3$.

National Research Council Canada (NRCC, Ottawa, Canada) sediment certified reference materials (CRMs) MESS-3 and MESS-4 and river water CRM SLRS-5, and National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) sediment SRM2702 and natural water SRM1640a were used for method validation. SRM981 Pb standard purchased from NIST was used for mass bias correction.

Isotope dilution sample preparation and analysis procedure. Sample preparation was undertaken in a class-100 clean room. For the determination of Pb in MESS-3, MESS-4 and SRM2702, 0.25 g subsamples of three replicates of each sediment were weighed into pre-cleaned Teflon vessels. Samples were then spiked with ^{207}Pb enriched spike so as to yield a ratio of ^{208}Pb/^{207}Pb near unity in the final digests. Thus, 0.37 g, 0.37 g and 2.3 g of 5.0 µg g^{-1} ^{207}Pb were added to MESS-3, MESS-4 and SRM2702 samples, respectively. Eight mL of HNO$_3$ and 1.0 mL of HF were then added to each vessel. Three sample blanks (spiked with 10 % of the amount of enriched spikes used for the samples) were processed along with samples. The sealed vessels were heated in the microwave oven using a 15 min

ramp and 25 min hold at 1400 W. After cooling, the caps were removed and the digests were transferred to pre-cleaned 50 mL Teflon tubes and evaporated in a 105°C block heater to near dryness. The final residues were treated with 10 mL 50 % (v/v) formic acid solution and heated at 90 °C for 30 min with caps on and diluted to 100 g with DIW. An aliquot of 0.070 g of 2542 μg g^{-1} Ni stock solution was added to each sample blank. A 10-fold dilution of NIST SRM2702 digests was performed prior to UV-PVG MC-ICPMS analysis. For reverse ID, three replicate 0.37 g solutions of 5.0 μg g^{-1} ^{207}Pb were accurately weighed into pre-cleaned polyethylene screw-capped bottles to which 0.52 g of 10.18 μg g^{-1} natural abundance Pb standard solutions was added such as to result in a ^{208}Pb/^{207}Pb ratio near 1. After addition of a 0.070g of 2542 μg g^{-1} Ni stock solution to each bottle, the contents were diluted to 100 g with 5% formic acid. A 0.10 μg g^{-1} NIST SRM981 Pb standard solution containing 0.070 g of the 2542 μg g^{-1} Ni stock solution in 5% formic acid was prepared and used to calculate a mass bias correction factor.

For natural river water SRM1640a, three replicates of 10 g solutions of SRM1640a were each spiked with 0.55g of 0.070 μg g^{-1} ^{207}Pb enriched spike so as to yield a ratio of ^{208}Pb/^{207}Pb near unity in the final solutions. After addition of 0.021g of 2542 μg g^{-1} Ni stock solution, 0.6 ml of formic acid was added to each bottle. Similarly, three replicate reverse ID solutions were prepared by accurately weighing 0.55 g of a 0.070 μg g^{-1} ^{207}Pb enriched spike and 0.27 g of a 0.4020 μg g^{-1} natural abundance Pb standard solution into pre-cleaned polyethylene screw-capped bottles. After addition of 0.021g of a 2542 μg g^{-1} Ni stock solution, the contents were diluted to 10 g with 5% formic acid.

Optimization of the Neptune MC-ICPMS was performed daily as recommended by the manufacturer. The instrument was tuned to achieve optimum sensitivity while maintaining flat topped peaks. In addition, measurements were only conducted after at least 1 hour of instrument warm-up time. Typical operating conditions are summarized in Table 1. The gain on each Faraday cup was monitored

daily to ensure normalization of its efficiency. The sample uptake tubing for the nebulizer was removed from solution while performing UV-PVG MC-ICPMS measurements. In addition, 0.04 M solution of BrCl was used to efficiently rinse the system between samples to eliminate memory effects. The samples and reverse spike ID calibration samples were subjected to on-line UV-PVG MC-ICPMS detection on the same day in an effort to achieve optimum results. Each solution was pumped at 1.2 mL min^{-1} for a minute to fill the PVG reactor, the sample was irradiated for 4 min by stopping the pump, and finally it was transported to the GLS and then to the ICP for detection by restarting the pump. Data acquisition started at sample solutions were irradiated about 3 min. Mass bias correction was implemented based on the NIST SRM981 Pb certified value for $^{208}Pb/^{207}Pb$ divided by its mean value determined in the standard. Static runs were employed to simultaneously monitor the two Pb isotopes using the Faraday cup configuration shown in Table 1. At the end of each run, acquired raw data were transferred to an off-line computer for further processing using Excel software. Instead of using peak areas characterizing the two Pb isotopes to generate the $^{208}Pb/^{207}Pb$ ratio, a more precise calibration based on linear regression of the transient intensities of the two Pb isotopes arising from the Pb peak was used for this purpose[LY1-4].

Table 1. Typical MC-ICPMS operating conditions

Instrument settings	
Rf power	1100 W
Plasma Ar gas flow rate	16.0 L min^{-1}
Auxiliary Ar gas flow rate	1.00 L min^{-1}
Neb gas flow rate	0.71 L min^{-1}
Sampler cone orifice (nickel)	1.00 mm
Skimmer cone orifice (nickel)	0.88 mm

Lens settings	Focus: -685 V; X deflection: 0.61 V; Y deflection: 2.43 V; Shape: 219 V; Rot Quad 1: 1.95 V; Foc Quad 1: -19.89 V; Rot Quad 2: 0.05 V; Source Offset: -8.0; Focus Offset: 50.00 V
Data acquisition parameters	
Zoom Optics	Focus Quad: 0 V and Dispersion Quad: 0 V
Scan type	Static
Faraday cup configuration	H3 (^{208}Pb); H2 (^{207}Pb)
Mass resolution, m/Δm at 5 and 95%	~300
Sensitivity	3.5 V/ppm for ^{208}Pb
Blank signal	0.1 mV for ^{208}Pb from 1% HNO3
Signal integration time	0.524 s
Number of integrations	1
Blocks/Cycles	1/600
	UV-PVG
Ar carrier gas flow rate for GLS	0.33 L min^{-1}

Standard additions sample preparation and analysis procedure. For comparison of results, standard additions calibration was applied for the determination of Pb in SLRS-5 and SRM1640a. Three sets of unspiked and spiked samples were prepared for both SLRS-5 and SRM1640a. Aliquots of 10g subsamples of each CRM were evaporated to dryness on a hot block at 105 °C and then redissolved in 2 mL of 25% formic acid. Proper amounts of a 0.4020 µg g^{-1} Pb standard solution were added to each spiked water sample to result in approximately a 1-, 2- and 4-fold increase in the Pb concentration. A mass of 0.021g of the 4273.9 µg g^{-1} Ni stock solution was added to each sample. The unspiked and spiked samples were then diluted to 10 g with DIW. The sample solutions were subjected to UV-PVG

MC-ICPMS detection as described earlier. The peak area of the ^{208}Pb isotope was used to construct a standard additions calibration curve for each sample.

Safety Considerations. The possible photochemically generated Pb species are unknown and potentially toxic, as may be those from co-generated species in real sample solutions. Proper ventilation and personal protective equipment should be employed for all manipulations.

RESULTS AND DISCUSSION

Optimization of UV-PVG for MC-ICPMS detection. During preliminary experiments, a 0.5 µg g^{-1} Pb standard solution containing 5% formic acid was continuously introduced to the PVG reactor at a flow rate of 1.0 mL min^{-1}. Only a background response for ^{208}Pb was detected (~1 mV), as shown in Figure 2a, whereas a sediment digest (0.25 g sediment digested and diluted to 100 g final solution) containing 0.06 µg g^{-1} Pb in 5% formic acid produced a signal of ~ 0.5 V for ^{208}Pb (Figure 2b). Only background signals for ^{208}Pb were detected when introducing solutions of 0.5 µg g^{-1} Pb containing formic acid ranging from 0 to 40%. These observations indicate that the constituents in the sample matrix (presence of other ions) significantly assist the UV-PVG reactions of Pb leading to formation of a volatile species. It was later noted that PVG of a simple Pb standard solution was indeed feasible if a modifier such as Ni^{2+} or Co^{2+} is deliberately added.
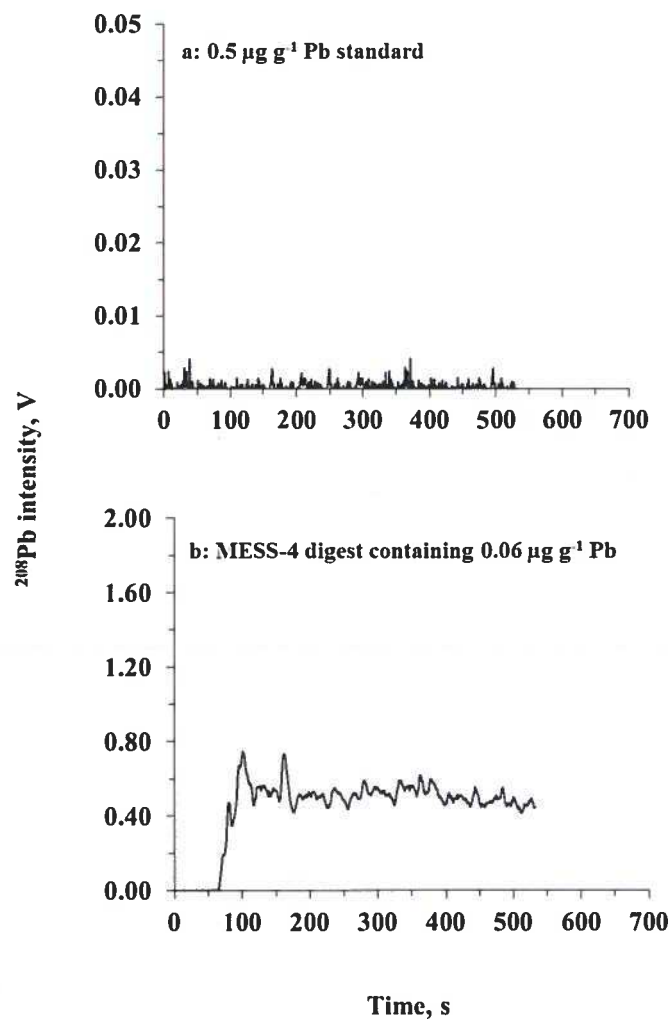
Figure 2. a:Temporal response arising from continuous introduction of a solution of 0.5 µg g^{-1} Pb in 5% formic; b: Temporal response arising from continuous introduction of a MESS-4 sediment digest containing 0.1 µg g^{-1} Pb in 5% formic acid..

The significance of this is discussed later. Subsequent experiments revealed that UV irradiation time has a significant effect on response. As shown in Figure 3a, a significantly higher transient Pb peak can be obtained if the same sediment digest containing 0.06 µg g^{-1} Pb in 5% formic acid is quickly delivered to fill the internal volume of the PVG reactor (0.8 mL) after which it was allowed to remain in the reactor (subsequently referred to as the "UV irradiation time") for controlled periods of time by stopping the

pump for varying intervals, after which it is delivered to the GLS at the same flow rate of 1.2 mL min^{-1} (subsequently referred to as the "sample transport flow rate"). Ar carrier gas flow rate to the GLS is linked to the nebulizer gas flow rate. Thus, both flow rates were optimized daily by continues introducing a digest of MESS-4 containing of 0.06 µg g^{-1} Pb in 5 % formic acid. Typical optimized nebulizer gas flow rate of 0.70 L min^{-1} and Ar carrier gas flow rate to the GLS of 0.33 L min^{-1} were used. Thus, three basic parameters potentially influencing PVG of Pb and its transport efficiency to the MC-ICPMS were optimized. These included the concentration of formic acid in the sample, irradiation time and sample transport flow rate.

The effect of formic acid concentration over the range 0 – 40 % in the sample on the response (peak area normalized to the maximum achieved) was investigated using a digest of MESS-4 containing of 0.06 µg g^{-1}Pb, while maintaining a 4 min irradiation time, nebulizer gas flow rate of 0.70 L min^{-1}, Ar carrier gas flow rate to the GLS of 0.33 L min^{-1} and sample transport rate of 1.0 mL min^{-1}. As shown in Figure 3b, response initially sharply increased as formic acid concentration increased from 0 to 2 %, thereafter the signal improvement was minimal and decreased beyond 7.5 %. In addition to formic acid, acetic acid and propionic acid were also tested for the PVG of Pb. Similarly, both responses of Pb from digests of MESS-4 containing of 0.06 µg g^{-1}Pb increased as the concentration of either acid increased from 0 to 5% and then decreased at higher concentrations. However, total Pb peak area response of 3.6 and 2.4 Vs at optimum 5% acetic and propionic acid concentrations were 70- and 110-fold lower, respectively, than the 260 Vs obtained when using 5% formic acid. Thus, samples adjusted to contain 5% formic acid were selected for all subsequent measurements to achieve maximum response. The lower response generated at higher concentrations may be the consequence of loss of penetration depth of the UV radiation into the sample as the absorption of the solution increases, an increase in possible

side reactions that do not lead to a volatile product, or enhanced photodecomposition of the product and its redissolution in the aqueous phase.

Figure 3.a: Temporal response from a digest of MESS-4 sediment containing 0.06 μg g^{-1} Pb in 5% formic, 4 min irradiation time, nebulizer gas flow rate of 0.70 L min^{-1}, Ar carrier gas flow rate to the GLS of 0.33 L min^{-1}, sample flow rate of 1.2 mL min^{-1}; b: Effect of formic acid concentration on response from Pb under above conditions (normalized signals).

The effect of UV irradiation time over the range 1 to 9 min was investigated using identical conditions expressed above but with the formic acid concentration fixed at 5 %. As shown in Figure 4b,

response initially sharply increased as irradiation time increased from 1 to 3 min, thereafter the signal improvement was minimal. The relatively slow kinetics of PVG of Pb means short irradiation time leads to insufficient yield. Thus, an irradiation time of 4 min was selected for all subsequent measurements to achieve maximum response and high sample throughput.

Transport pump flow rate determines how quickly the irradiated sample solution containing the generated volatile Pb species is delivered to the GLS from the PVG reactor. The effect of sample delivery flow rate was evaluated in the range $0.3 - 1.8$ mL min^{-1}. A digest of MESS-4 containing of 0.06 µg g^{-1} Pb in 5% formic acid with 4 min irradiation time was used for this purpose with all other conditions constant. As evident from Figure 4b, peak area optimum response (normalized to the maximum achieved) is essentially independent of the delivery rate of sample to the GLS, as expected, since this parameter does not influence the generation efficiency and reflects only the total mass of analyte delivered to the GLS. Peak height does exhibit an optimum response, which occurs at $1.2 - 1.8$ mL min^{-1} as it is essentially controlled by sample dispersion. The peak becomes very broad at low flow rates and produces a narrow transient at higher flow rates, as expected. A transport pump flow rate of 1.2 mL min^{-1} was selected for all subsequent measurements in consideration of both maximum response and sufficient data points (40 data points at selected flow rate) to accurately define the Pb peak for accurate measurements.

Figure 4. a: effect of UV irradiation time on the response of Pb (normalized peak area); b: impact of sample transport rate on the response of Pb (■: peak height ●: peak area).

Modifier assisted UV-PVG. Although the mechanism of HG of PbH_4 is still debated, it is evident that the presence of suitable oxidizing agents facilitate plumbane generation, resulting in significant improvements product yield[19, 31]. For this purpose, H_2O_2 and $Cr_2O_7^{2-}$ were investigated to determine their impact on the PVG of Pb from a Pb 0.050 µg g^{-1} standard solution in 5% formic acid using a 4 min

UV irradiation time. Neither reagent significantly improved the PVG efficiency of Pb. The impact of addition of various transition metal ions (Mn^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+} and Fe^{3+}, typically present in a real sample matrix) on the PVG of Pb was also investigated. The presence of Mn^{2+} and Zn^{2+} did not enhance PVG efficiency, whereas Cu^{2+} was found to significantly suppress the signal. As shown in Figure 5 (peak area quantitated), both Ni^{2+}(Fig 5a: ●) and Co^{2+}(Fig. 5b) significantly improve the PVG of Pb. The presence of Fe^{3+} did likewise, but the enhancement was found to be 18-fold lower than that arising from use of Ni^{2+}. This effect is similar to that of adding transition metal ions to the conventional HG for plumbane generation[32]. Nickel and Co considerably enhanced the efficiency of Pb chemical HG using a mixture of HNO_3 and H_2O_2 as an oxidant, possibly giving rise to formation of an unstable convalent hydride favoring plumbane formation[33, 34]. Although not elucidated here, the PVG of Pb may undergo parallel processes as a consequence of enhanced charge transfer reactions assisted by the presence of added metal ions. In our study, significant amounts of volatile Ni species (probably Ni carbonyl) were observed simultaneously under the same condition for Pb detection. Further investigation of the mechanism may improve our understanding of the technique, but it is beyond the scope of the current study. Thus, Ni^{2+} was selected as the modifier for all subsequent measurements in consideration of it yielding both maximum response at minimum concentration (see below).
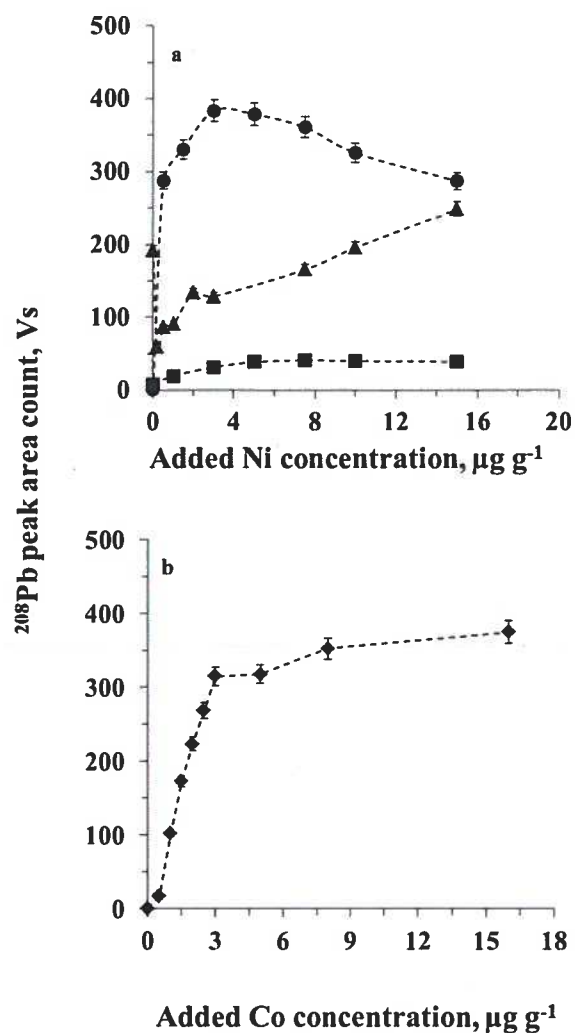
Figure 5. Effect of added metal ions on response from Pb. a: Ni, ●0.10 µg g^{-1} Pb standard solution in 5% formic acid, ■digest of MESS-4 containing 0.01 µg g^{-1} Pb in 5% formic acid, ▲ digest of MESS-4 containing 0.06 µg g^{-1} in 5% formic acid; b: addition of Co to 0.10 µg g^{-1} Pb standard solution in 5% formic acid.

The effect of added Ni^{2+} on response from a sediment digest of MESS-4 was investigated using optimized conditions of 4 min irradiation time, nebulizer gas flow rate of 0.70 L min^{-1}, Ar carrier gas flow rate to the GLS of 0.33 L min^{-1} and a sample transport rate of 1.2 mL min^{-1}. As shown in Figure 5a

■, response slowly increased over the range of Ni^{2+} concentration $0 - 16$ µg g^{-1}, while response (Fig. 5a

▲) from a digest of MESS-4 containing 0.06 µg g^{-1} in 5% formic acid had sharply decreased at

Ni^{2+} concentration of 0.5 µg g^{-1} and then increased at higher Ni^{2+} concentration values.   These

observations indicate the influence of matrix constituents present in the MESS-4 digest on the PVG of

Pb. When a more diluted digest is used, added Ni^{2+} is beneficial. As a result of these observations, Ni^{2+}

modifier was thus not added to the sediment digests (based on 0.25g digested to a final of 100g) for any

subsequent measurements.

Figures of Merit. Under the optimized experimental conditions, a 15-fold improvement in sensitivity

was obtained using the PVG compared to that for direct solution nebulization (relative sample uptake

rates of 1.2 and 0.1 mL min^{-1}, respectively). This illustrates one of the advantages of vapour generation

in that the mass flux of sample to the detector can be increased in two ways – *via* the intrinsic enhanced

efficiency with which the analyte is delivered and also because the sample can be delivered at a much

greater flow rate without compromising introduction efficiency. This figure is based on the ratio of the

integrated response from a 30s wide Pb peak obtained using PVG sample introduction compared to the

integrated signal comprising a 30s time slice of the steady-state signal generated from the same sample

obtained using solution nebulization. A relatively good precision of 4.0 % RSD was obtained from

replicate measurements of a standard solution of 0.075 µg g^{-1} Pb in 5% formic acid under optimized

conditions, shown in Figure 6b. Since the sample matrix has a significant effect on the PVG of Pb,

external calibration may only be confidently applicable to samples of a relatively simple matrix, such as

artic snow[14, 15].

A method detection limit of 0.005 ng g^{-1} for Pb is estimated based on three times the standard

deviation of Pb concentration obtained from method blank containing 5% formic acid when using the

external calibration. This LOD is superior to a value of 0.07 ng g^{-1} obtained using direct sample introduction based on solution nebulization, and is 16-fold lower than that achieved by HG AFS (0.08 ng g^{-1}) [35] but compatible with that reported for HG ICPMS (0.003 ng g^{-1})[35]. The linear range of the proposed method runs from 0.005 - 100 ng g^{-1} Pb, as shown in Figure 6a, with deviations from linearity occurring at concentration of 200 ng g^{-1}. Sample throughput with the current system is relatively low, primarily as a consequence of the selected irradiation time desired for maximum PVG efficiency. Similarly, the proposed method also suffers memory effects similar to those reported for HG ICPMS[35]. After each analysis, a solution of 0.04 M BrCl was used to rinse the UV-PVG system for 1 min. This efficiently eliminated all carryover. With an overall sample processing time of approximately 6 min (2.5 min with direct liquid introduction), a throughput of 10 samples per hour can be achieved.
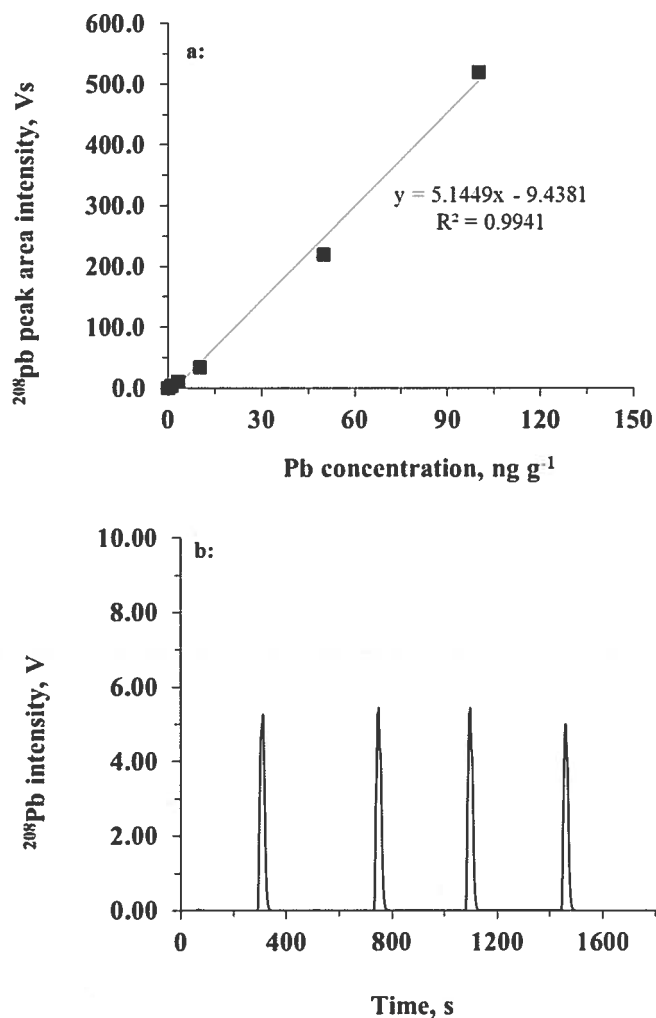
Figure 6. a: external calibration curve generated with Pb standard solutions; b: repeat measurements of a 50 ng g^{-1} Pb standard solution in 5% formic acid and containing 3 μg g^{-1} Ni^{2+}.

Determination of Pb in river waters. Since HNO$_3$ often has an adverse effect on the PVG of many analytes, as noted for Fe and Ni[36], its effect on the response from Pb was investigated. As shown in Figure 7, significant suppression is evident when the concentration of HNO$_3$ exceeds 0.01%. Since natural water CRMs are acidified with HNO$_3$ to enhance their long-term stability,
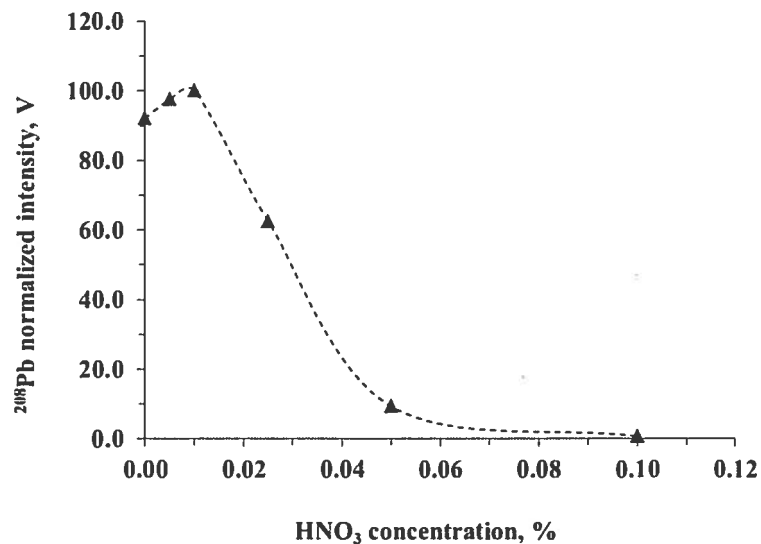
Figure 7. The effect of HNO_3 concentration on the response from 50 ng g^{-1} Pb in 5 % formic acid and containing 3 µg g^{-1} Ni^{2+}.

samples of NRC SLRS-5 and NIST 1640a were evaporated on a hot block to remove and HNO_3 and then redissolved in 5% formic acid prior to PVG. To compensate for matrix effects, a standard additions calibration approach was applied for the determination of Pb in these natural waters. Additions of approximately 1-, 2- and 4-fold the endogenous Pb concentration were made. The correlation coefficients of the standard additions calibration curves for Pb over the concentration range of 0.08 to 100 ng g^{-1} were great than 0.99. Results obtained are summarized in Table 2 and are in agreement with certified values, confirming the accuracy of the methodology.

Table 2. Determination of Pb in natural waters and sediments

Sample and calibration method	Determined, ng g^{-1} (1SD, n=3)	Certified, ng g^{-1} (U, 95% or k=2)

NRC SLRS-5 (Std. Add.)	0.080±0.006	0.081±0.006
NIST 1640a (Std. Add.)	12.06±0.48	12.005±0.040
NIST 1640a (ID)	12.02±0.05	12.005±0.040
Sample and calibration method	**Determined, µg g^{-1}** (1SD, n=3)	**Certified, µg g^{-1}** (U, 95% or k=2)
MESS-3 (ID)	21.60±0.06	21.1±0.7
MESS-4 (ID)	21.43±0.08	21.1±1.8
SRM 2702(ID)	132.4±0.2	132.8±1.1

Subsequent experiments were performed using isotope dilution methodology for comparison purposes and to explore the ultimate capabilities of the methodology. the following equation was used for quantitation of Pb in NIST SRM1640a river water[13]:

$$C = C_z \cdot \frac{m_y}{m_x} \cdot \frac{m_z}{m'_y} \cdot \frac{A_y - B_y \cdot R_n}{B_{xz} \cdot R_n - A_{xz}} \cdot \frac{B_{xz} \cdot R'_n - A_{xz}}{A_y - B_y \cdot R'_n} \cdot \frac{A_r(X)}{A_r(Z)} \tag{1}$$

where C is the concentration of Pb in the sample (ng g^{-1}); C_z is the concentration of primary assay standard (ng g^{-1}); m_y is the mass of spike used to prepare the blend solution of sample and spike (g); m_x is the mass of sample used (g); m_z is the mass of primary assay standard (g); m'_y is the mass of spike used to prepare the blend solution of spike and primary assay standard solution for reverse ID (g); A_y is the abundance of the reference isotope in the spike; B_y is the abundance of the spike isotope in the spike; A_{xz} is the abundance of the reference isotope in the sample or primary assay standard; B_{xz} is the abundance of the spike isotope in the sample or primary assay standard; R_n is the measured reference/spike isotope ratio (mass bias corrected) in the blend solution of sample and spike; R'_n is the measured reference/spike isotope ratio (mass bias corrected) in the blend solution of spike and primary assay standard, $A_r(X)$ is the atomic weight of the analyte element in the sample and $A_r(Z)$ is the atomic

weight of the analyte element in the primary assay standard.

Instead of using the peak areas of the ^{208}Pb and ^{207}Pb isotopes to generate a ^{208}Pb/^{207}Pb ratio, a more precise calibration[37-40] based on linear regression of the transient intensities of the two Pb isotopes was used to derive this quantity. As shown in Figure 8, the slope of a plot of ^{208}Pb intensities versus ^{207}Pb intensities using data characterizing the entire peak (165-195 seconds, shown in Fig. 3a) provides the measured ratio of ^{208}Pb/^{207}Pb. A value of 12.02 ± 0.05 ng g^{-1} (1SD, n=3) was obtained for Pb in SRM1640a, in agreement with the certified value. Clearly, measurement precision of 0.42 % RSD obtained for Pb using double isotope dilution is superior to the 4.0 % RSD obtained using standard additions calibration.
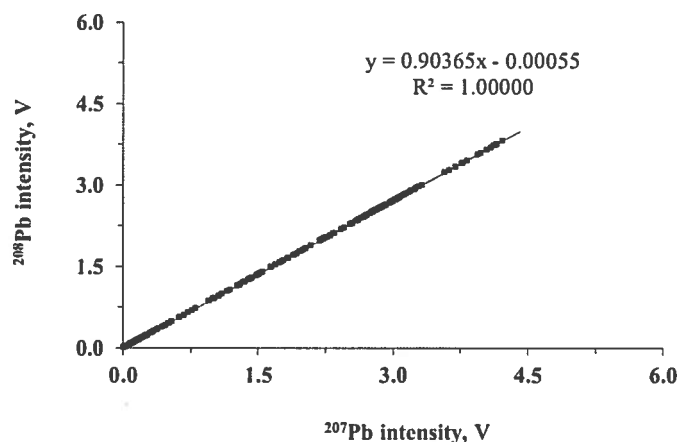

Figure 8. Intensity of ^{208}Pb versus intensity of ^{207}Pb across the Pb peak (data from 100 % peak used) of a spiked MESS-4 digest. The slope of the linear regression corresponds to the ^{208}Pb/^{207}Pb ratio.

Quantitation of Pb in sediments. Double ID was applied to the determination of Pb concentrations in sediment materials using the developed PVG MC-ICPMS method. Results for three sediment CRMs are summarized in Table 2 and are in good agreement with certified values. Associated precisions of

determination in a range of 0.15 to 0.37 % RSD are obtained in three sediment samples, superior to currently reported precisions for Pb measurements in sediments or soils[41].

CONCLUSION

A novel and sensitive approach is developed for the accurate and precise determination of Pb in environmental samples using transition metal ion-assisted PVG for sample introduction with MC-ICPMS detection. A 15-fold improvement in sensitivity is realized using PVG compared to that for direct solution nebulization. The method provides a detection limit of 0.005 ng g^{-1} for Pb, a 14-fold improvement over direct solution nebulization, and comparable to that for chemical HG ICPMS. However, the proposed methodology is simpler with lower blank and consumption of reagents. The mechanism of PVG of Pb is not clear and detailed investigations may improve our understanding of this technique and be used to find a means to accelerate the kinetics of the photochemical reaction. Nevertheless, the proposed method has great potential for analysis of trace Pb in a variety of materials.

REFERENCES

1.   Cheng, H.; Hu, Y., Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: A review. *Environmental Pollution* 2010, *158*, (5), 1134-1146.

2.   Company, R.; Serafim, A.; Lopes, B.; Cravo, A.; Shepherd, T. J.; Pearson, G.; Bebianno, M. J., Using biochemical and isotope geochemistry to understand the environmental and public health implications of lead pollution in the lower Guadiana River, Iberia: A freshwater bivalve study. *Science of the Total Environment* 2008, *405*, (1-3), 109-119.

3.   Edwards, M., Fetal Death and Reduced Birth Rates Associated with Exposure to Lead-Contaminated Drinking Water. *Environmental Science & Technology* 2014, *48*, (1), 739-746.

4.   Wang, J. H.; Yu, Y. L.; Du, Z.; Fang, Z. L., A low cost and sensitive procedure for lead screening in human whole blood with sequential injection-hydride generation-atomic fluorescence spectrometry. *Journal of Analytical Atomic Spectrometry* 2004, *19*, (12), 1559-1563.

5.   Boeckx, R. L., Lead poisoning in children. *Analytical Chemistry* 1986, *58*, (2), 274A-[288A].

6.   Yang, Y.; Pathirathna, P.; Siriwardhane, T.; McElmurry, S. P.; Hashemi, P., Real-Time Subsecond Voltammetric Analysis of Pb in Aqueous Environmental Samples. *Analytical Chemistry* 2013, *85*, (15), 7535-7541.

7.   Edwards, M.; Triantafyllidou, S.; Best, D., Elevated Blood Lead in Young Children Due to Lead-Contaminated Drinking Water: Washington, DC, 2001-2004. *Environmental Science & Technology* 2009, *43*, (5), 1618-1623.

8.   Clark, B.; Masters, S.; Edwards, M., Profile Sampling To Characterize Particulate Lead Risks in Potable Water. *Environmental Science & Technology* 2014, *48*, (12), 6836-6843.

9.   Chen, K.; Huang, L.; Yan, B.; Li, H.; Sun, H.; Bi, J., Effect of Lead Pollution Control on Environmental and Childhood Blood Lead Level in Nantong, China: An Interventional Study. *Environmental Science & Technology* 2014, *48*, (21), 12930-12936.

10.   Soto-Jimenez, M. F.; Hibdon, S. A.; Rankin, C. W.; Aggarawl, J.; Ruiz-Fernandez, A. C.; Paez-Osuna, F.; Flegal, A. R., Chronicling a century of lead pollution in Mexico: Stable lead isotopic composition analyses of dated sediment cores. *Environmental Science & Technology* 2006, *40*, (3), 764-770.

11.   Haug, G. H.; Hughen, K. A.; Sigman, D. M.; Peterson, L. C.; Rohls, U., Atlantic water flow pathways revealed by lead contamination in Arctic basin sediments. *Science* 2001, *293*, (5533), 1301-4.

12.   Hill, S., Inductively Coupled Plasma Spectrometry and its Applications, 2nd Edition. *Blackwell Publishing, Oxford, UK* 2007, 98-121.

13.   Yang, L.; Sturgeon, R. E., High accuracy and precision isotope dilution mass spectrometry: An application to the determination of Mo in seawater. *Journal of Analytical Atomic Spectrometry* 2009, *24*, (10), 1327-1335.

14.   Krachler, M.; Zheng, J.; Fisher, D.; Shotyk, W., Direct Determination of Lead Isotopes (206Pb, 207Pb, 208Pb) in Arctic Ice Samples at Picogram per Gram Levels Using Inductively Coupled Plasma-Sector Field MS Coupled with a High-Efficiency Sample Introduction System. *Analytical Chemistry* 2004, *76*, (18), 5510-5517.

15.   Rosman, K. J. R.; Chisholm, W.; Boutron, C. F.; Candelone, J. P.; Gorlach, U., Isotopic evidence for the source of lead in Greenland snows since the late 1960s. *Nature* 1993, *362*, (6418), 333-335.

16.   Wu, P.; He, L.; Zheng, C.; Hou, X.; Sturgeon, R. E., Applications of chemical vapor generation in non-tetrahydroborate media to analytical atomic spectrometry. *Journal of Analytical Atomic Spectrometry* 2010, *25*, (8), 1217-1246.

17.   Thompson, K. C.; Thomerso.Dr, ATOMIC-ABSORPTION STUDIES ON DETERMINATION OF ANTIMONY, ARSENIC, BISMUTH, GERMANIUM, LEAD, SELENIUM, TELLURIUM AND TIN BY UTILIZING GENERATION OF COVALENT HYDRIDES. *Analyst* 1974, *99*, (1182), 595-601.

18.   Deng, B.; Xu, X.; Xiao, Y.; Zhu, P.; Wang, Y., Understanding the effects of potassium ferricyanide on lead hydride formation in tetrahydroborate system and its application for determination of lead in milk using hydride generation inductively coupled plasma optical emission spectrometry. *Analytica Chimica Acta* 2015, *853*, 179-186.

19.   Yilmaz, V.; Arslan, Z.; Rose, L., Determination of lead by hydride generation inductively coupled plasma mass spectrometry (HG-ICP-MS): On-line generation of plumbane using potassium hexacyanomanganate(III). *Analytica Chimica Acta* 2013, *761*, 18-26.

20.   Chen, H.; Tang, F.; Gu, C.; Brindle, I. D., The influence of chelating reagents on plumbane generation: Determination of lead in the presence of PAN-S. *Talanta* 1993, *40*, (8), 1147-1155.

21.   Zhang, S. Z.; Han, H. B.; Ni, Z. M., DETERMINATION OF LEAD BY HYDRIDE GENERATION ATOMIC-ABSORPTION SPECTROMETRY IN THE PRESENCE OF NITROSO-R SALT. *Analytica Chimica Acta* 1989, *221*, (1), 85-90.

22.   D'Ulivo, A.; Mester, Z.; Meija, J.; Sturgeon, R. E., Mechanism of generation of volatile hydrides of trace elements by aqueous tetrahydroborate(III). Mass spectrometric studies on reaction products and intermediates. *Analytical Chemistry* 2007, *79*, (7), 3008-3015.

23.   D'Ulivo, A.; Onor, M.; Spiniello, R.; Pitzalis, E., Mechanisms involved in chemical vapor generation by aqueous tetra hydroborate(III) derivatization - Role of hexacyanoferrate(III) in plumbane generation. *Spectroc. Acta Pt. B-Atom. Spectr.* 2008, *63*, (8), 835-842.

24.	Huang, K.; Xia, H.; Li, M.; Gao, Y.; Zheng, C.; Hou, X., Improved hydride generation-atomic fluorescence spectrometry for determination of trace lead: minimization of blank from potassium ferricyanide. *Analytical Methods* **2012**, *4*, (12), 4058-4062.

25.	Chuachuad, W.; Tyson, J. F., Determination of lead by flow injection hydride generation atomic absorption spectrometry with tetrahydroborate immobilized on an anion-exchange resin. *Journal of Analytical Atomic Spectrometry* **2005**, *20*, (4), 282-288.

26.	Petrov, P. K.; Wibetoe, G.; Tsalev, D. L., 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. *Spectrochimica Acta Part B-Atomic Spectroscopy* **2006**, *61*, (1), 50-57.

27.	Guo, X. M.; Sturgeon, R. E.; Mester, Z.; Gardner, G. J., Vapor generation by UV irradiation for sample introduction with atomic spectrometry. *Analytical Chemistry* **2004**, *76*, (8), 2401-2405.

28.	Zheng, C.; Sturgeon, R. E.; Brophy, C.; Hou, X., Versatile Thin-Film Reactor for Photochemical Vapor Generation. *Analytical Chemistry* **2010**, *82*, (7), 3086-3093.

29.	Yin, Y. G.; Liu, J. F.; Jiang, G. B., Photo-induced chemical-vapor generation for sample introduction in atomic spectrometry. *Trac-Trends Anal. Chem.* **2011**, *30*, (10), 1672-1684.

30.	Sturgeon, R. E.; Willie, S. N.; Mester, Z., UV/spray chamber for generation of volatile photo-induced products having enhanced sample introduction efficiency. *Journal of Analytical Atomic Spectrometry* **2006**, *21*, (3), 263-265.

31.	Karadjova, I. B.; Lampugnani, L.; D'Ulivo, A.; Onor, M.; Tsalev, D. L., Determination of lead in wine by hydride generation atomic fluorescence spectrometry in the presence of hexacyanoferrate(III). *Analytical and Bioanalytical Chemistry* **2007**, *388*, (4), 801-807.

32.	Madrid, Y.; Camara, C., LEAD HYDRIDE GENERATION ATOMIC-ABSORPTION SPECTROMETRY - AN ALTERNATIVE TO ELECTROTHERMAL ATOMIC-ABSORPTION SPECTROMETRY. *Analyst* **1994**, *119*, (8), 1647-1658.

33.	Bonilla, M.; Rodriguez, L.; Camara, C., DETERMINATION OF LEAD IN BIOLOGICAL-MATERIALS BY ATOMIC-ABSORPTION SPECTROMETRY SENSITIZED WITH HYDRIDE GENERATION. *Journal of Analytical Atomic Spectrometry* **1987**, *2*, (2), 157-161.

34.	Madrid, Y.; Bonilla, M.; Camara, C., LEAD HYDRIDE GENERATION - EFFICIENCY IN PERSULFATE - NITRIC-ACID MEDIUM AND APPLICATION TO THE DETERMINATION OF LEAD IN BIOLOGICAL SAMPLES. *Journal of Analytical Atomic Spectrometry* **1988**, *3*, (8), 1097-1100.

35.	Chen, S. Y.; Zhang, Z. F.; Yu, H. M.; Liu, W. Q.; Sun, M., Determination of trace lead by hydride generation-inductively coupled plasma-mass spectrometry. *Analytica Chimica Acta* **2002**, *463*, (2), 177-188.

36.	Zheng, C. B.; Yang, L.; Sturgeon, R. E.; Hou, X. D., UV Photochemical Vapor Generation Sample Introduction for Determination of Ni, Fe, and Se in Biological Tissue by Isotope Dilution ICPMS. *Analytical Chemistry* **2010**, *82*, (9), 3899-3904.

37.	Fietzke, J.; Liebetrau, V.; Guenther, D.; Guers, K.; Hametner, K.; Zumholz, K.; Hansteen, T. H.; Eisenhauer, A., An alternative data acquisition and evaluation strategy for improved isotope ratio precision using LA-MC-ICP-MS applied to stable and radiogenic strontium isotopes in carbonates. *Journal of Analytical Atomic Spectrometry* **2008**, *23*, (7), 955-961.

38.	Epov, V. N.; Berail, S.; Jimenez-Moreno, M.; Perrot, V.; Pecheyran, C.; Amouroux, D.; Donard, O. F. X., Approach to Measure Isotopic Ratios in Species Using Multicollector-ICPMS Coupled with Chromatography. *Analytical Chemistry* **2010**, *82*, (13), 5652-5662.

39.	Ying Gao, R. E. S., Zoltán Mester, Raphael Galea, Patrick Saull, Xiandeng Hou and Lu Yang, UV Photochemical Vapor Generation Determination of Cu in Biological Tissues using Isotope Dilution Multi-collector Inductively Coupled Plasma Mass Spectrometry. *Anal. Chem.* **2014**, *Submitted*.

40.	Angel Rodriguez-Castrillon, J.; Garcia-Ruiz, S.; Moldovan, M.; Garcia Alonso, J. I., Multiple linear regression and on-line ion exchange chromatography for alternative Rb-Sr and Nd-Sm MC-ICP-MS isotopic measurements. *Journal of Analytical Atomic Spectrometry* **2012**, *27*, (4), 611-618.

41.	Maleki, N.; Safavi, A.; Ramezani, Z., Determination of lead by hydride generation atomic absorption spectrometry (HGAAS) using a solid medium for generating hydride. *Journal of Analytical Atomic Spectrometry* **1999**, *14*, (8), 1227-1230.