



Analytical note

Chemical vapor generation sample introduction for the determination of As, Cd, Sb, Hg, and Pb in nail polish by inductively coupled plasma mass spectrometry

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ABSTRACT

This paper describes a flow injection vapor generation (VG) method using inductively coupled plasma mass spectrometry (ICP-MS) for determining As, Cd, Sb, Hg, and Pb in nail polish. The samples for VG were prepared as aqueous slurries of a nail polish (0.5% m/v), thiourea (1% m/v), Co(II) ($0.75 \mu\text{g mL}^{-1}$), and HCl (1.2% v/v). Chemical VG of As, Cd, Sb, Hg, and Pb ions, by reduction with tetrahydroborate (3% m/v in 0.2% m/v NaOH), enabled their separation from the slurry. With VG sample introduction, As, Cd, Sb and Hg signals were increased by 1–2 orders (except Pb) compared to solution nebulization due to better sample introduction. Quantifications were performed by VG ICP-MS using isotope dilution and standard addition methods as slopes of calibration plots of analytes in the slurries were higher. Using the reported procedure, samples of three nail polishes purchased locally were analyzed for their levels of As, Cd, Sb, Hg, and Pb. The results obtained were in good agreement with those measured using electrothermal vaporization ICP-MS. In the original nail polish sample, the detection limits, calculated as 3σ of blank measurements, for As, Cd, Sb, Hg, and Pb, estimated from standard addition curves, were 0.06, 0.12, 0.14, 0.2, and 12 ng g^{-1} , respectively.

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1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is an attractive technique for elemental and isotopic analyses because it combines the remarkable atomization and ionization of analytes present in injected sample solutions into the inductively coupled plasma (ICP) with the high sensitivity and selectivity of mass spectrometry (MS). Though the technique is meant for solution nebulization that offers good stability, sample transport is inefficient, with <3% of the sample being introduced into the plasma. Accordingly, the coupling of alternative sample introduction systems with ICP-MS can extend its applicability to a greater range of analytical challenges. For example, vapor generation (VG) is a technique suitable for interfacing with ICP-MS [1–8]. As a result of improved sample introduction, the sensitivities of vapor-forming elements can increase greatly when the vapors from a VG system are introduced into the ICP that also avoid matrix based spectral or non-spectral interference [5,9–11]. The flow injection (FI) mode of vapor introduction is a particularly facile means of coupling with

ICP-MS [12,13]. In the present study, a simple laboratory-built VG system was used to transfer gaseous hydrides into the plasma for FI ICP-MS [8].

Cosmetics are encountered widely in our daily lives. Because they are applied directly to sensitive parts of the body, toxic elements in the cosmetics can have detrimental effects on human health. Hence, cosmetics must pass through stringent quality controls. Moreover, some of the toxic metals found in cosmetics are subject to the act of Taiwan's Food and Drug Administration. The maximum concentrations of As, Cd, Hg, and Pb allowed by the Taiwanese government in cosmetics are 3, 20, 1, and $10 \mu\text{g g}^{-1}$, respectively. ICP-MS has been used to determine the levels of trace elements in a wide range of cosmetic samples [14–18], with most of these analyses requiring tedious sample dissolution and pretreatment steps [19]. In this study, we combined slurry sampling of nail polish with VG ICP-MS, adopted to analyse complex environmental samples, which avoid sample dissolution [20–23].

Accordingly, we have developed an accurate and rapid slurry sampling FI ICP-MS method, employing a VG system, for the determination of As, Cd, Sb, Hg, and Pb in nail polish samples. We studied effects of the slurry preparation and VG conditions on the sensitivity and applied the method for the determination of As, Cd, Sb, Hg, and Pb in selected nail polish samples.

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2. Experimental section

2.1. Apparatus and conditions

An ELAN 6100 DRC II ICP-MS instrument (PE-SCIEX, Concord, ON, Canada) and a HGA 600MS electrothermal vaporizer (ETV) equipped with Model AS 60 autosampler and an USS 100 ultrasonic slurry sampler were used for all measurements.

An in-house continuous-flow VG system with a six-port injection valve (Rheodyne type 50) and a 100- μL sample loop was coupled with ICP-MS for the determination of As, Cd, Sb, Hg, and Pb using FI analysis [8]. A schematic representation of the FI vapor generator system is available in Fig. S1 (Appendix); a detailed description of the working principle of this vapor generator is available elsewhere [8]. Vapors generated from the sample slurries in VG system were introduced into the ICP torch through Teflon tubing. The operating conditions for the VG and ICP systems were optimized using the FI method. A nail polish slurry (0.5% m/v) spiked with As (0.5 ng mL⁻¹), Cd (30 ng mL⁻¹), Sb (0.2 ng mL⁻¹), Hg (1 ng mL⁻¹), Pb (10 ng mL⁻¹), thiourea, Co(II), and HCl was selected as the model to optimize the operating conditions of the VG system. The concentrations of thiourea, Co(II), and HCl in the injected sample and carrier solution, the concentration of NaBH₄, and the flow rates were optimized to obtain the maximum signal for As, Cd, Sb, Hg, and Pb. The operating conditions for the VG and ICP-MS systems are summarized in Table 1. The accuracy has been verified by comparing values obtained by the present procedure with values obtained by alternative procedures such as total digestion procedure and ETV-ICP-MS [24] using Student's *t*-test. A MARS 6 microwave digester (CEM, Matthews, NC) was employed to digest the nail polish samples.

2.2. Reagents

All reagents were of analytical reagent grade; deionized water was used throughout. The reagents and standard solutions were purchased from following sources: Suprapur HNO₃, Suprapur HCl, NaBH₄, NaOH, potassium antimony(III) oxide tartrate hemihydrate, thiourea, ascorbic acid, and As(V), Co, and Cl element standard solutions from Merck (Darmstadt, Germany); sodium arsenite (NaAsO₂) from Alfa (Danvers, MA, USA); potassium hexahydroxy antimony(V) and antifoam Y-30 from Sigma Chemicals (St. Louis, MO, USA); Mo standard solution from Fisher Scientific (Fair Lawn, NJ, USA); W and Hg element standard solutions from SPEX CertiPrep (Metuchen, NJ, USA); and Cd and Pb

element standard solutions from AccuStandard (New Haven, CT, USA). Enriched isotopes were purchased from the following sources: ¹¹¹CdO (96.4%) from Oak Ridge National Laboratory (Oak Ridge, TN, USA); ¹²³Sb (97.1%) and ²⁰¹HgO (80.5%) from Cambridge Isotope Laboratories (Andover, MA, USA); and ²⁰⁶Pb (NO₃)₂ (99.7%) from Merck (Darmstadt, Germany).

Nail polish samples purchased in local market are containing isopropyl alcohol, butyl and ethyl acetates, citrates along with usual polymers such as nitro cellulose, glycol copolymer.

2.3. Sample preparation

Three nail polish samples (ruby, tangerine, fluorescent pink) were considered for analysis. Samples were present as syrupy liquids from which sampling has been done. Sample preparation should consider to convert As and Sb to +3 and Pb to +4 states for better VG efficiency. Furthermore, due the difference in sensitivities of As, Cd, Sb, Hg, and Pb in slurry and aqueous solution the samples were analyzed using standard addition and isotope dilution methods. A portion (0.05 g) of the nail polish was placed in a 10-mL flask and then thiourea (0.1 g) and HCl (0.12 mL) were added. The slurry was diluted with water to 5 mL and then heated at 75 °C for 30 min in a water bath to reduce As(V) and Sb(V) to As(III) and Sb(III), respectively [25]. After cooling, Co(II) (75 $\mu\text{g mL}^{-1}$, 0.2 mL) was added, followed by antifoam Y-30 (3 drops). After introducing suitable quantities of the enriched isotopes or As, Cd, Sb, Hg, and Pb element standard solutions (six-point calibration; 0–2 ng mL⁻¹ for As, Cd, Sb, and Hg; 0–20 ng mL⁻¹ for Pb), the slurry was diluted with pure water to 10 mL. The final slurry contained 0.5% m/v of nail polish, 1% m/v of thiourea, 0.75 $\mu\text{g mL}^{-1}$ of Co(II), and 1.2% v/v of HCl. A blank solution was also prepared, as outlined above, to correct any analyte in the reagents used for sample preparation. The slurry was found to be stable for 5–10 min. As and when sample is withdrawn for analysis it was shaken thoroughly and hence no change in the analysis was observed. Aliquots (100 μL) of these slurries were subjected to VG for the determination of As, Cd, Sb, Hg, and Pb by ICP-MS. Quantification was performed using an approach described previously for isotope dilution [26] and/or standard addition calibration curves.

For ETV-ICP-MS, slurry prepared was containing 2% m/v nail polish, 0.5% m/v tartaric Acid, 0.5% m/v thioacetamide, 0.2% m/v Triton X-100 and 0.5% v/v HNO₃.

To determine total analyte concentrations using the complete dissolution method, the nail polish samples (0.4 g each) were weighed in closed Teflon PFA vessels and then HNO₃ (3 mL) and HF (1 mL) were added. The mixture was digested in a single stage using a microwave power and pressure of 1200 W and 800 Psi. Temperature used was 200 °C with ramp and hold times of 25 and 20 min respectively. HF was also added for complete recovery of analytes of interest [27]. The dissolved nail polishes were diluted to 100 mL each for their introduction into the ICP-MS system. Dilution factors used for total dissolution and VG are 250 and 200 respectively. The concentrations of As, Cd, Sb, Hg, and Pb were quantified through external calibration with an internal standard (Rh, 1 ng mL⁻¹).

3. Results and discussion

3.1. Selection of VG conditions

Transition metal ions can decrease the efficiency of VG [5,28]. Some nail polishes would be added with different transition metals to acquire different colors. Masking agents such as thiourea [29] and ascorbic acid [30] were tested to solve this problem. Though ascorbic acid did not yield any significant improvement in ion signals, the addition of thiourea (1% m/v) enhanced the signals of the As, Cd, Sb, and Hg ions simultaneously. All the optimization studies have been carried out on nail polish slurries spiked with standards. We examined the effect of the

Table 1
Operating conditions of ICP-MS, VG System and Microwave Digester.

ICP-MS instrument	PerkinElmer SCIEX ELAN 6100 DRC II
ICP-MS parameters	
RF power	1000 W
Plasma gas flow rate	15.0 L min ⁻¹
Auxiliary gas flow rate	1.325 L min ⁻¹
Nebulizer gas flow rate	1.1 L min ⁻¹
Mass spectrometer settings	
Resolution	0.7 amu at 10% peak maximum
Dwell time	50 ms
Sweeps	12
Readings	100
Replicates	1
Autolens	On
VG conditions	
Sample loop volume	100 μL
NaBH ₄	3% m/v in 0.2% m/v NaOH
Carrier	1% m/v thiourea and 0.75 $\mu\text{g mL}^{-1}$ Co(II) in 1.2% v/v HCl
Flow rate of solution	1.15 mL min ⁻¹
Volume of mixing coil	135 μL (0.76 mm id \times 30 cm length)
Slurry sample	0.5% m/v nail polish, 1% m/v thiourea, 0.75 $\mu\text{g mL}^{-1}$ Co(II), and 1.2% v/v HCl

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