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# Slurry sampling flow injection chemical vapor generation inductively coupled plasma mass spectrometry for the determination of trace Ge, As, Cd, Sb, Hg and Bi in cosmetic lotions

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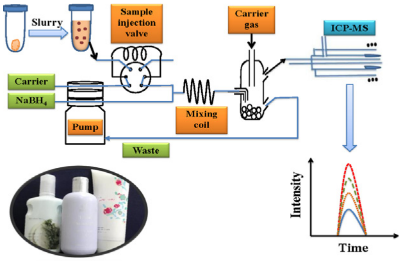
## HIGHLIGHTS

- Determination of Ge, As, Cd, Sb, Hg and Bi in cosmetic lotions in a single run.
- Accurate analysis using isotope dilution and standard addition methods.
- Vapor generation ICP-MS yielded superior detection limits compared to ETV-ICP-MS.
- No sample dissolution increased sample through put.
- Analysis of GBW09305 Cosmetic (Cream) reference material for accuracy.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A slurry sampling inductively coupled plasma mass spectrometry (ICP-MS) method has been developed for the determination of Ge, As, Cd, Sb, Hg and Bi in cosmetic lotions using flow injection (FI) vapor generation (VG) as the sample introduction system. A slurry containing 2% m/v lotion, 2% m/v thiourea, 0.05% m/v L-cysteine, 0.5 $\mu$g mL$^{-1}$ Co(II), 0.1% m/v Triton X-100 and 1.2% v/v HCl was injected into a VG-ICP-MS system for the determination of Ge, As, Cd, Sb, Hg and Bi without dissolution and mineralization. Because the sensitivities of the analytes in the slurry and that of aqueous solution were quite different, an isotope dilution method and a standard addition method were used for the determination. This method has been validated by the determination of Ge, As, Cd, Sb, Hg and Bi in GBW09305 Cosmetic (Cream) reference material. The method was also applied for the determination of Ge, As, Cd, Sb, Hg and Bi in three cosmetic lotion samples obtained locally. The analysis results of the reference material agreed with the certified value and/or ETV-ICP-MS results. The detection limit estimated from the standard addition curve was 0.025, 0.1, 0.2, 0.1, 0.15, and 0.03 ng g$^{-1}$ for Ge, As, Cd, Sb, Hg and Bi, respectively, in original cosmetic lotion sample.

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## 1. Introduction

Inductively coupled plasma mass spectrometry (ICP-MS) is a technique for elemental and isotopic analysis that combines ICP for atomization and ionization with sensitivity and selectivity of mass spectrometry. The sample introduction based on pneumatic nebulization though offers good stability, sample introduction is inefficient. Hence, efforts have been made to couple alternative sample introduction systems to ICP-MS to extend its application range. The type of analytical tasks that can be solved by ICP-MS can be extended using a number of other sample introduction techniques that are compatible with ICP-MS. Vapor generation (VG) is one such technique that is being employed in ICP-MS [1–8]. Several studies have shown that the sensitivity and detection limits of vapor-forming elements are greatly improved when they are introduced into the plasma as vapors [9]. It was also shown that appropriate vapor generation conditions can be used to remove or separate the analyte from problematic matrix species, which would otherwise cause spectral and non spectral interferences [5,10]. Additional advantage is, a set of hydride forming elements can be analyzed together in a sample using a multi-element technique such as ICP-MS. Vapor introduction in flow injection mode is a simple and rapid technique that has been coupled to ICP-MS previously [11,12].

Cosmetics have become a part in the life of humans and are being applied for cleansing, beautifying, promoting attractiveness, or to enhance the appearance. Though they contain mainly useful organic compounds along with water, oils and emulsifying agents, there is a possibility of contamination with toxic inorganic compounds/elements during manufacturing process. As they are directly applied on sensitive parts of the body, presence of toxic elements in cosmetics causes detrimental effects on human health. Hence, cosmetics need to pass through stringent quality control with respect to toxic element content. Moreover, some of these elements are the subject of food and drug legislation. For instance, according to the regulations of Taiwan government, the maximum allowed concentration of As, Cd, Hg and Pb in cosmetics is 3, 20, 1 and 10 $\mu g\,g^{-1}$, respectively. Thus, the determination of trace elements in cosmetics, in order to measure the levels of toxic elements, is important. ICP-MS has been applied for the determination of trace elements in various cosmetic samples [13–17]. Most of the analyses need tedious sample dissolution and pretreatment steps [18]. In this work, a slurry sampling technique combined with vapor generation ICP-MS has been proposed as an alternative for avoiding the need for sample dissolution or mineralization steps [19–21]. We reported slurry sampling in combination with ETV-ICP-MS for the determination of Cu, As, Cd, Sb, Hg, Pb and Bi in sun screens [22]. However, such procedures require selection of suitable chemical modifier either to volatilize analytes or to reduce volatility of matrix element and also optimization of ashing and vaporization temperatures. Hence, simpler procedures with superior detection limits are desirable. Moreover, sample analysis time of ETV is much higher compared to chemical vapor generation.

The aim of the present work is to develop accurate and rapid slurry sampling flow injection (FI) ICP-MS method with a vapor generation sample introduction device for the determination of Ge, As, Cd, Sb, Hg and Bi in cosmetic lotions. Effect of slurry preparation on ion signal and optimization studies for the vapor generation of Ge, As, Cd, Sb, Hg and Bi are reported. This method has been applied for the determination of Ge, As, Cd, Sb, Hg and Bi in selected lotion samples.

## 2. Experimental

### 2.1. Apparatus and conditions

An ELAN 6100 D RC II ICP-MS instrument (PE-SCIEX, Concord, ON, Canada) was used for this study. Vapors generated from samples, after passing through the vapor generation system, were introduced into the ICP torch through Teflon tubing. The operating conditions for the vapor generation and the ICP were optimized by the flow injection method. In this study, a cosmetic lotion slurry spiked with suitable amount of Ge, As, Cd, Sb, Hg and Bi was selected as the model to optimize the operating conditions. The vapor generation system and the ICP conditions were selected to maximize the signal-to-background ratio for the analytes, when a slurry was injected into the ICP by flow injection vapor generation system. The vapor generation and ICP-MS operating conditions used in this work are summarized in Table 1. A MARS microwave digester (CEM, Matthews, NC) was used to digest the lotion samples to analyse them by solution nebulization for cross validation purpose.

In this study, a laboratory-built continuous-flow vapor generation system was coupled with ICP-MS for the determination of Ge, As, Cd, Sb, Hg and Bi using FI analysis [8]. It was assembled from a six-port injection valve (Rheodyne type 50) with a 100 $\mu$L sample loop. Vapor generated from the VG system was delivered to the ICP-MS system for Ge, As, Cd, Sb, Hg and Bi determination via

**Table 1**
Equipment and conditions.

| | |
|---|---|
| ICP-MS instrument | PerkinElmer-SCIEX ELAN6100 DRC II |
| ICP parameters | |
| RF power | 1050 W |
| Plasma gas flow rate | 15.0 L min$^{-1}$ |
| Auxiliary gas flow rate | 1.325 L min$^{-1}$ |
| Nebulizer gas flow rate | 0.95 L min$^{-1}$ |
| Mass spectrometer settings | |
| Resolution | 0.7 amu at 10% peak maximum |
| Dwell time | 50 ms |
| Sweeps | 5 |
| Readings | 250 |
| Replicates | 1 |
| Autolens | On |
| CVG condition | |
| Sample loop volume | 100 $\mu$L |
| $NaBH_4$ | 5.0% m/v in 0.2% m/v NaOH |
| Carrier | 2.0% m/v thiourea, 0.05% m/v L-cysteine, 0.5 $\mu g\,mL^{-1}$ Co(II) in 1.2% v/v HCl |
| Flow rate of $NaBH_4$ and carrier solutions | 0.95 mL min$^{-1}$ |
| Volume of mixing coil | 160 $\mu$L (1 mm i.d. × 20 cm length) |
| Slurry sample | 2% m/v lotion, 0.1% m/v Triton X-100, 2.0% m/v thiourea, 0.05% m/v L-cysteine, 0.5 $\mu g\,mL^{-1}$ Co(II), 1.2% v/v HCl |