



Direct determination of mercury in cosmetic samples by isotope dilution inductively coupled plasma mass spectrometry after dissolution with formic acid

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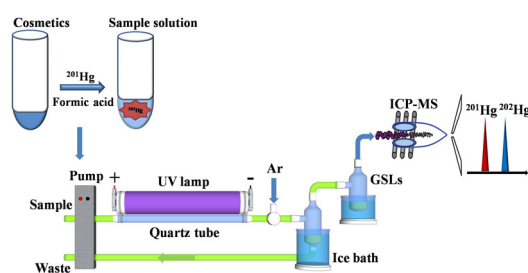
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HIGHLIGHTS

- Simple, sensitive, and accurate method is established for mercury determination in cosmetics.
- The sample preparation procedure is highly simplified.
- Isotope dilution efficiently eliminates matrix effect.
- First report of using formic acid based method in combination with PVG-ID-ICP MS for mercury quantitation in cosmetics.

GRAPHICAL ABSTRACT



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ABSTRACT

A new method was proposed for the accurate determination of mercury in cosmetic samples based on isotopic dilution (ID)-photochemical vapor generation (PVG)-inductively coupled plasma mass spectrometry (ICP MS) measurement. Cosmetic samples were directly dissolved in formic acid solution and subsequently subjected to PVG for the reduction of mercury into vapor species following by ICP MS detection. Therefore, the risks of analyte contamination and loss were avoided. Highly enriched ²⁰¹Hg isotopic spike is added to cosmetics and the isotope ratios of ²⁰¹Hg/²⁰²Hg were measured for the quantitation of mercury. With ID calibration, the influences originating from sample matrixes for the determination of mercury in cosmetic samples have been efficiently eliminated. The effects of several experimental parameters, such as the concentration of the formic acid, and the flow rates of carrier gas and sample were investigated. The method provided good reproducibility and the detection limits were found to be 0.6 pg mL⁻¹. Finally, the developed method was successfully applied for the determination of mercury in six cosmetic samples and a spike test was performed to verify the accuracy of the method.

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1. Introduction

Cosmetics are used worldwide by most of the population. The use of skin lightening cosmetics has becoming a common practice for women to obtain a lighter skin tone or remove the freckles

[1,2]. The application of mercurial preparations to the skin has been accepted for centuries in cosmetic products [1,3,4]. Organic mercury forms such as phenyl mercuric acetate are sometimes used as cosmetic preservatives in eye make-up; while inorganic mercury, such as ammoniated mercury, are the active ingredients in skin bleach creams for their purported skin-lightening and anti-freckle effects [5–7]. However, mercury is one of the most toxic elements impacting on human health. Exposure of mercury can cause the damage of the brain, heart, kidney, stomach, and intestines even at

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very low concentrations [8–10]. Therefore, mercury compounds are prohibited to use in cosmetic products now. The US Food and Drug Administration (USFDA) stated recently that cosmetics should contain no more than $1 \mu\text{g g}^{-1}$ of mercury as unavoidable impurities under conditions of good manufacturing practice. Despite this, the public continue to have access to these cosmetic products with mercury concentration above the maximum permissible amount, sporadic cases as well as outbreaks of inorganic mercury poisoning still occur [5,6,11,12].

Many analytical techniques have been reported for the determination of mercury in biological and environmental samples [13–16]. However, the research focusing on the sample pretreatment and analysis of mercury in cosmetics is scarce [17–20]. Recently, a new method was reported for the speciation of mercury in liquid cosmetic samples by ionic liquid based dispersive liquid–liquid microextraction with high-performance liquid chromatography (HPLC)-inductively coupled plasma mass spectrometry (ICP MS) detection [21]. Inorganic mercury was found as the main species in the investigated liquid cosmetic samples, which accorded with the previous research results [2,22]. For the determination of total mercury in cosmetic products, time-consuming and tedious sample treatments are always required. Typically, acid-based sample digestion procedure prior to instrumental detection are recommended [17]. The combinations of strong acid, oxidant, and high temperature and pressure are often involved in the sample decomposition process. However, sample contamination arising from the use of large amount of reagents and the loss of analyte during the volatilization may result in poor detection limits and large detection errors. Alternatively, the use of organic solvents including formic acid and tetramethylammonium hydroxide (TMAH) as tissue solubilizers for the analysis of biological samples are also suggested [23–26]. The sample preparation methods allow simplifying sample treatment procedure and reducing work times, which in turn increases the analysis throughput. Additionally, without heating, the risk of mercury loss during the volatilization process in acid digestion can be efficiently avoided. However, the analytical application of formic acid/TMAH related method for the analysis of cosmetic samples have not yet been explored.

Cold vapor generation (CVG) using tetrahydroborate (THB) or SnCl_2 as a reductant coupled to atomic spectrometry including atomic absorption spectrometry (AAS), atomic fluorescence spectrometry (AFS) as well as ICP MS is the most popular approach for trace Hg determination [27–31]. However, in many cases, interferences from transition metals often decrease the sensitivity and reproducibility, leading to poor analytical results. Moreover, contamination from THB reagent and the instability of its solution limit the dynamic linear concentration range. Besides, the toxicity and low vapor generation efficiency restrict the wide application of the SnCl_2 system. Commercial Mercury Analyzer (MA), which integrates combustion/electrothermal vaporization of the sample and preconcentration of mercury by amalgamation with gold trap followed by AAS, is developed for the direct, sensitive and rapid determination of mercury in solid samples. The integrated analytical procedure makes it much more convenient for mercury determination than conventional digestion-based methods. In spite of this, when dealing with the sample with high organic content, the background correction system is often inefficient [32–34]. Furthermore, to obtain the accurate analysis results, the certified reference materials are usually needed for the accuracy check or even construction of the matrix-matched calibration curve for sample analysis with different weights [35,36]. But due to the complicated sample matrices of cosmetics, matrix-matched certified reference materials are not always available.

Photochemical vapor generation (PVG) utilizing free radicals generated by photo-redox reactions as reductant is a green sample introduction method for mercury determination [37–39]. Hg^{2+}

can be efficiently converted into Hg^0 in the presence of low molecular weight organic compounds (e.g., alcohol, formic acid, acetic acid or formaldehyde) with UV irradiation. Compared to conventional CVG, PVG is a simple, environmental friendly, cost-efficient and with high efficiency and fewer interferences from transition metals [40]. The use of PVG system facilitates the determination procedure of mercury by making use of the low molecular weight organic compounds as the dissolution reagent for cosmetic samples, which can be also served as the photo assisted reductant in PVG for mercury. It provides the possibility of analyzing mercury in cosmetic samples with minimal reagent and simple analytical procedure. However, the large molecular weight organic compounds in sample matrix would quench the available reductive radicals in PVG and the opaque slurry solution will reduce the penetration efficiency of UV radiation [41,42]. It would be in turn influence the mercury vapor generation efficiency in cosmetic sample solution, leading to poor analytical results by external calibration detection.

In this paper, a new method was proposed for the determination of ultra-trace mercury concentration in cosmetic samples based on isotopic dilution (ID)-PVG-ICP MS measurement after dissolution in formic acid solution. ID-ICP MS is capable of compensating for any loss of analyte during sample preparation, for suppression of ion intensities by concomitant compounds present in the sample matrix and for instrument drift, providing isotopic equilibrium is achieved between the added spike and the endogenous analyte in the sample [39,43]. The concentrated isotope of ^{201}Hg was used as the diluter for the determination of mercury in cosmetics by isotopic dilution, as the use of the isotope ratio of $^{202}\text{Hg}/^{201}\text{Hg}$ for mercury detection is more sensitive compared to those of using other isotope ratios. Coupling ID-ICP MS with PVG after dissolution with formic acid will provide a simple, sensitive and reliable method for mercury determination in cosmetic samples. Formic acid was used not only to assist the photoreduction but also to solubilize the cosmetic samples, the risks of analyte loss and sample contamination has been thus greatly decreased.

2. Experimentation

2.1. Instrument

An ELAN DRCTM-e ICP MS (Perkin Elmer, Inc., Shelton, CT, USA) equipped with quartz torch and alumina sample injector tube was used. The fitted Gem Tip cross-flow nebulizer and a corrosion resistant double pass Ryttons spray chamber mounted outside the torch box were replaced by a PVG-system for mercury determination in this work. Optimization of the ELAN DRCTM-e was performed as recommended by the manufacturer. Optimum detection conditions for PVG were investigated independently. The instrument dead time was obtained by measuring the $^{204}\text{Pb}/^{206}\text{Pb}$ ratio in standard solutions at different concentration levels, and was found to be 50 ns. Isotopes of ^{201}Hg and ^{202}Hg were simultaneously monitored. Operating conditions are summarized in Table 1.

A schematic of the PVG system hyphenated to the ICP MS is shown in Fig. 1. A model FIA-3110 flow injection system (Vital Instruments Co. Ltd., Beijing, PR China) was used for the solution sample introduction in the PVG system. A low-pressure Hg vapor UV lamp (15W, Philips Co., Holland), fitted with a quartz tube (15 cm \times 1.8 mm i.d. \times 2.8 mm o.d.), was employed as the PVG reactor. For operation convenience, the PVG reactor was wrapped with aluminum foil to protect the operator from UV radiation and minimize ozone formation. After reduction by photo reactor, sample solution was pumped through a tandem set of two gas–liquid separators (GLSs). The generated mercury vapor was stripped from sample solution and directed to the ICP MS using an argon carrier stream from Ar sample gas channel of ELAN DRCTM-e. The tandem

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