



# Development of a cosmetic cream certified reference material: Certification of lead, mercury and arsenic mass fractions in cosmetic cream



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## ABSTRACT

This paper describes the development of a cosmetic cream certified reference material containing lead, mercury and arsenic. High accuracy exact matching isotope dilution mass spectrometry or standard addition method was used for the assignment of certified values and long-term stability study. A multiple spiking approach was employed to simplify the analytical procedure. The metal contents were found to be homogenous and stable for a period of 14 days at 46°C (short-term stability) and over a period of at least 6 months at ambient temperature (long-term stability). A metrological approach was used to consider potential biases to achieve appropriate accuracy for the certified mass fraction values. The expanded relative uncertainties at 95% confidence level for lead ( $26.14 \text{ mg/kg} \pm 0.76 \text{ mg/kg}$ ), mercury ( $2.956 \text{ mg/kg} \pm 0.092 \text{ mg/kg}$ ) and arsenic ( $5.25 \text{ mg/kg} \pm 0.28 \text{ mg/kg}$ ) were 2.90%, 3.11% and 5.38%, respectively.

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## 1. Introduction

The use of cosmetics and personal care products as a means to improve skin quality and appearance is well accepted globally. Although toxic elements are banned as intentional ingredients in cosmetics, they may exist as impurities either as contaminants in the raw ingredients or as by-products of the manufacturing process [1,2]. As toxic elements in cosmetic products may be ingested or absorbed through skin, they can accumulate in the body over time and cause adverse health effects even at low levels [3,4]. The toxic elements of most concern include lead (Pb), mercury (Hg) and arsenic (As). Lead can affect almost every system in the human body, including the reproductive, neurological, hematopoietic, hepatic and renal systems [5]. In children, long term low level exposure is harmful for the brain and nervous system [6,7]. Chronic exposure to inorganic mercury may cause peripheral neuropathy, encephalopathy and interstitial renal disease [8]. Arsenic exposure is believed to increase risk of lung, bladder, kidney, as well as skin cancers. It has also been suggested to cause hypertension and cardiovascular disease [7].

As awareness on the safety of cosmetic products arises, organisations around the world have started the initiative to test commercially available cosmetic products to evaluate their toxic element contents [9–11]. Environment Defence Canada has carried out a testing, where out of the 49 different face makeup products tested, 20% were found to contain arsenic and 96% to contain lead [12]. In the Middle East, where kohl (eye make-up) is commonly used, lead poisoning is very common, especially in children [13]. Kohl is also widely used in India, Pakistan and some parts of Africa. Elevated mercury level was also found in skin lightening soaps and creams [8]. In the 1960s to 1980s, there had been a few reports on mercury-containing skin-whitening creams; most of them came from Africa or the Middle East [14–16]. In the 1990s, there was an outbreak of mercury poisoning associated with Mexican beauty cream [17,18] and also a reported case of mercury poisoning associated with mercury-containing soap in Kenya [19]. In Hong Kong, unregistered skin cream from China was associated with suspected mercury poisoning in about 100 women [20,21].

Therefore, different regions around the world have established relevant regulations to safeguard the safety of consumers. The ASEAN Harmonized Cosmetic Regulatory Scheme signed in 2003 provides a common definition for cosmetics and details of the ingredients that cannot be used in cosmetics' as well as listings of permitted preservatives, UV absorbers and colourants [22]. Similarly, USA, European Union and Canada have established toxic

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element impurity limits. US Food and Drug Administration (FDA) has set a limit for lead concentration of 10–20 mg/kg in cosmetic colour additives [23]. A guidance for lead, mercury and arsenic levels in cosmetic products was set by the Health Canada to be lower than 10, 3 and 3 mg/kg, respectively [24] and by the German Federal Government to be lower than 20, 1 and 5 mg/kg, respectively [25].

From the safety perspective, certified reference materials (CRMs) or reference materials (RMs) of cosmetic products are important to uphold legislation in different countries and to ensure customers' safety. From the analysis perspective, they are useful for method validation or as quality control materials, allowing testing laboratories to improve the accuracy of the test results. However, there are currently very few available cosmetic CRMs in the market. Therefore, it is timely to produce a CRM for toxic elements in a cosmetic matrix.

This paper describes the development of a cosmetic cream CRM containing lead, mercury and arsenic by the Health Sciences Authority of Singapore (HSA), a designated institute (DI) for chemical metrology in Singapore. To demonstrate its measurement capability, HSA participated in an international comparison (CCQM-K106: Pb, As and Hg measurements in cosmetic cream) prior to establishing the certified mass fraction values for the toxic elements in the CRM [26]. The results obtained by HSA were in good agreement with other National Metrology Institutes (NMIs) and DIs.

The development of the CRM, including procedures for sample preparation, homogeneity study, stability study, assignment of certified values and uncertainty evaluation, was carried out according to the requirements of ISO Guides 34 and 35 [27,28]. Homogeneity and short-term stability studies for the three elements were carried out using external calibration, while assignment of certified values and long-term stability study were carried out using high accuracy exact matching isotope dilution mass spectrometry (IDMS) (for Pb and Hg) [29] or standard addition (for As) [30] method. Microwave-assisted acid digestion techniques using different acids were also explored.

## 2. Experimental

### 2.1. Reagents, standard and spike solutions

All experimental work was carried out in class 100 low laminar flow fumehoods or a class 10,000 clean room. Standard and sample solutions were prepared gravimetrically on a microanalytical balance (Mettler Toledo XP205 or XP26, Greifensee, Switzerland).

Nitric acid (67–70% HNO<sub>3</sub>, PlasmaPure, SCP Science), which was distilled twice using DST-1000 sub-boiling distillation system (Saville Corporation, MN, USA), hydrogen peroxide (30–32% H<sub>2</sub>O<sub>2</sub>, PlasmaPURE Plus), hydrochloric acid (32–35% HCl, PlasmaPURE Plus), hydrofluoric acid (47–51% HF, PlasmaPURE Plus) and Milli-Q element water (18.2 MΩ cm, Millipore Corporation, MA, USA) were used for sample preparation. All working solutions were diluted with 5% HNO<sub>3</sub> (aq). Working solutions for mercury measurement were diluted with 4% HNO<sub>3</sub> + 1% HCl (aq). The calibration standard and the spike solutions were prepared from the certified reference standards and enriched isotopes listed in Table 1. The certified reference standards were obtained from the National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA). The isotopically enriched isotopes were obtained from the Oak Ridge National Laboratory (Oak Ridge, USA).

The cosmetic cream sample for the international comparison (CCQM-K106) was provided by the National Institute of Metrology (NIM), China. The approximate concentration levels for lead,

**Table 1**  
Certified reference standards and isotope spikes used.

Element	Certified reference standard		Isotope spike (Isotopic fraction)
	Code	Certified value (mg/g)	
Pb	SRM 3128	9.995 ± 0.014	<sup>206</sup> Pb (99.76%)
	SRM 981 <sup>a</sup>	–	
Hg	SRM 3133	9.954 ± 0.053	<sup>201</sup> Hg (96.17%)
As	SRM 3103a	9.999 ± 0.015	–
Ga	SRM 3119a <sup>b</sup>	10.00 ± 0.04	–

<sup>a</sup> Used for mass bias correction.

<sup>b</sup> Used as internal standard.

mercury and arsenic were 5–10 mg/kg, 0.1–2 mg/kg and 1–10 mg/kg, respectively.

### 2.2. Instrumentations

Microwave-assisted digestion of the cosmetic cream was performed using a microwave digester (Milestone Ethos 1, Milestone S.r.l., Sorisole, Italy) equipped with a carousel holding ten Teflon digestion vessels. Table 2 shows the operating conditions of the microwave digester.

Agilent Technologies 7700x ICP-MS system (ICP-qMS) (Agilent Technologies International Japan, Ltd., Tokyo, Japan) equipped with an octopole collision cell was used for isotope ratio measurements for lead and mercury. Intensity ratio measurements for arsenic and confirmation of results for lead and mercury were carried out using a Finnigan Element 2 (Finnigan MAT GmbH, Bremen, Germany) sector-field ICP-MS (SF-ICP-MS) using a self-aspirating PFA MicroFlow nebulizer. The instruments were optimised daily as recommended by the manufacturers to achieve optimum sensitivity and stability. The typical operating conditions and data acquisition parameters are summarised in Table 3.

### 2.3. Preparation of candidate CRM sample

The cream base was formulated using ingredients suitable for use in cosmetics and it met the ASEAN Cosmetic Directive. Known amounts of heavy metals (PbNO<sub>3</sub> (aq), Na<sub>2</sub>H(AsO<sub>4</sub>) (aq) and HgCl<sub>2</sub> (aq)) and a stabiliser were spiked into the cream emulsion and homogenised by mixing with a PTFE-coated propeller stirrer for 30 min. The cream was then packaged into pre-cleaned amber glass bottles (approximately 10 g of cream in each bottle). Each bottle was labelled according to its dispensing sequence number. A total of ninety bottles were prepared. The targeted ranges of concentration of lead, mercury and arsenic in the cosmetic cream were 20–30 mg/kg, 0.1–5 mg/kg and 2–8 mg/kg, respectively.

### 2.4. Homogeneity study, stability study and assignment of reference values

The homogeneity of the material was established after bottling and storing the samples at 18–25 °C. Nine bottles were chosen using a stratified random sampling scheme. The samples were analysed by ICP-MS using external calibration. The homogeneity of each

**Table 2**  
Operating condition of the microwave digester.

Parameter	Value
Power/W	1000
Temperature/°C	190
Ramp time/min	15
Hold time/min	25
Cool down time/min	30

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