

ARTICLE

Mercury Determination at Ultra-trace Level in Eye Shadow by a New Electrothermal Vaporization System Coupled to ICP-MS

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Solid sampling-electrothermal vaporization inductively coupled plasma mass spectrometry (SS-ETV-ICP-MS) was proposed for ultra-trace determination of Hg in eye shadow samples. The ETV system was optimized using a heating program, consisting of drying at 80 °C for 20 s and vaporization at 800 °C for 10 s, followed by cooling for 120 s, without a pyrolysis step. The carrier gas flow rate was set to 1.10 L min⁻¹, and sample mass up to 4 mg was analyzed. An alternative external calibration strategy using a standard solution of Hg and magnesium silicate for matrix matching demonstrated good linearity (R^2 0.9983) in

the range of 5 to 100 pg of Hg. Magnesium silicate enhances analyte transport and acts as a modifier, enabling calibration with aqueous standard solutions and presenting an alternative to certified reference material (CRM). Despite the differences in signal profiles for Hg observed in the eye shadow samples, CRM MESS-3 (Marine Sediment), and the standard solution, the method has good accuracy when the signal was integrated using peak area. Compared to cold vapor inductively coupled plasma mass spectrometry, which needs acid digestion and a ten-fold dilution with a limit of quantification (LOQ) of 0.1 µg g⁻¹ Hg, the SS-ETV-ICP-MS provided a significantly lower LOQ (0.001 µg g⁻¹) and a simplified analytical approach for Hg determination. This approach presents a practical alternative for determining Hg in eye shadows at ultra-trace levels.

Cite: Silva, J. S.; Henn, A. S.; Mello, G. M.; Dressler, V. L.; Flores, E. M. M. Mercury Determination at Ultra-trace Level in Eye Shadow by a New Electrothermal Vaporization System Coupled to ICP-MS. *Braz. J. Anal. Chem.* 2025, 12 (48), pp 295-308. <http://dx.doi.org/10.30744/brjac.2179-3425.AR-173-2024>

Submitted November 6, 2024, Resubmitted January 17, 2025, 2nd time Resubmitted March 6, 2025, 3rd time Resubmitted April 30, 2025, Accepted May 5, 2025, Available online May 23, 2025.

This article was submitted to the BrJAC special issue celebrating the achievement of Journal Impact Factor.

Keywords: eye shadow, cosmetic, Hg, solid sampling, ETV-ICP-MS

INTRODUCTION

Cosmetics, particularly eye shadows, are widely used products that may contain potentially toxic elements as impurities.^{1,2} Studies have found different amounts of metals in cosmetics, such as Pb, Co, Ni, Cr, As, and Hg.²⁻⁵ The presence of potentially toxic elements, such as Hg, presents serious concerns regarding the safety of these products due to their detrimental impacts on human health.³ Exposure to Hg can lead to adverse effects, including allergic reactions, neurotoxicity, and systemic impairment, depending on the route of exposure and dosage.^{1,6-8} Additionally, the thin skin of the eyelids is particularly susceptible to the absorption of toxic substances due to its structure and proximity to the eyes, which increases the risk of contamination.^{3,8} According to the Brazilian Health Regulatory Agency (ANVISA), Hg and its compounds should not be used in makeup and makeup removers for the eye area.⁹ The European Union also restricts the concentration of Hg in cosmetics.¹⁰ The United States Food and Drug Administration (FDA) enforces strict regulations prohibiting the presence of Hg in cosmetics, with an exception for its use as a preservative in eye-area products, where the concentration must not exceed 65 $\mu\text{g g}^{-1}$ and only if no adequate and safe non-mercurial substitute is available.^{8,11}

Studies have identified the presence of Hg and other metals (As, Cd, Cr, Co, Pb, Ni) in eye shadows from various countries.^{3,8,12} A study performed in Turkey reported Hg concentrations exceeding 1 $\mu\text{g g}^{-1}$ in some cosmetic products, such as eye shadows, blush, and lipsticks.¹³ Research by Ahmed et al. analyzed 21 popular brands of eye shadows from China, France, Italy, and Ireland, purchased markets in Riyadh, Saudi Arabia.¹⁴ The products were classified into three price categories: low, medium, and high. In low-cost eye shadows, Hg concentrations ranged from 0.24 to 7.42 $\mu\text{g g}^{-1}$, with an average of 3.04 $\mu\text{g g}^{-1}$. Medium-cost products contained Hg levels between 2.94 and 8.24 $\mu\text{g g}^{-1}$, averaging 4.49 $\mu\text{g g}^{-1}$. High-cost eye shadows contained Hg from 1.83 to 10.00 $\mu\text{g g}^{-1}$, with an average of 4.96 $\mu\text{g g}^{-1}$.¹⁴ Furthermore, the study examined 150 cosmetic products across 12 categories to quantify As, Cd, Cr, Co, Pb, Ni by inductively coupled plasma mass spectrometry (ICP-MS), and Hg by cold vapor atomic fluorescence spectrometry (CV AFS). Median concentrations of As (0.21 $\mu\text{g g}^{-1}$), Cr (3.1 $\mu\text{g g}^{-1}$), Co (0.91 $\mu\text{g g}^{-1}$), Pb (0.85 $\mu\text{g g}^{-1}$), and Ni (2.7 $\mu\text{g g}^{-1}$) were reported. At the same time, Cd and Hg were below the limits of detection (LOD, 0.018 $\mu\text{g g}^{-1}$ for Cd and 0.001 $\mu\text{g g}^{-1}$ for Hg).¹⁵ Metals, including Hg, may be present in eye shadows as impurities originating from mineral components such as mica, talc, clays, and pigments. These contaminants likely result from raw materials or manufacturing processes, with the intentional addition of Hg to enhance product preservation.^{3,8,12,16} Therefore, the presence of Hg and other toxic metals in eye shadows highlights the need for strict monitoring.

The main analytical method for Hg determination is by cold vapor atomic absorption spectrometry (CV AAS)¹⁷⁻²⁰ and CV AFS,^{15,18,20,21} as well as inductively coupled plasma optical emission spectrometry (ICP OES)^{16,20,22} and ICP-MS.^{16,17,22} The CV AAS is a relatively accessible and widely used technique and is known for its low cost and simple instrumentation. However, interferences in vapor generation may arise from the matrix, such as transition metals. Additionally, the physical properties of the solution, moisture during vapor generation, and gas phase interferences can impact the Hg determination.^{16,22} The CV AFS is ideal for detecting Hg at very low levels (1 ng g^{-1}), making it widely used in environmental analyses.¹⁵ However, as in CV AAS, CV AFS requires using the same reagents, and interferences can occur.²¹ The ICP OES and ICP-MS techniques enable multielement determination, wide linear range, and low limits of quantification (LOQs)^{16,23} whereas ICP-MS provides a lower LOQ and higher precision than ICP OES and is capable of detecting Hg at ultra-trace levels.^{8,16}

One of the main limitations of Hg determination techniques based on ICP-MS and ICP OES, which generally use pneumatic nebulization, is the need to convert solid samples into a solution and the associated memory effect.^{16,20} This demands a preliminary sample preparation step, which may involve acid digestion, microwave-assisted digestion, microwave-induced combustion, liquid-phase extraction, solid-phase microextraction, or ultrasound-assisted extraction.^{16,20,24-26} In addition, sample preparation in

open systems has limitations, such as the potential loss of Hg due to volatilization and contamination, which can compromise the accuracy and precision of the results.²⁰

As an alternative to sample preparation, direct solid sampling techniques can be used for Hg determination in eye shadows, addressing the challenges associated with sample preparation.^{16,27} Techniques such as high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GFAAS) have been used for Pb and Cd determination in eye shadows and lipstick as an alternative to sample preparation.^{27–29} Commercially available direct Hg analyzers (DMAs) have been evaluated in cosmetic samples, demonstrating efficiency and reliability for quantifying Hg in various products, including lipsticks, mascaras, eye shadows, and eyebrow pencils, with minimal sample handling.¹² Electrothermal vaporization (ETV) coupled to ICP-MS has also been successfully used to determine Hg and other elements, achieving low LOD (0.8 ng g^{-1}).^{30,31} Additionally, a study utilized palladium nanoparticles as a modifier for Hg determination in vegetable oil using ETV-ICP-MS, achieving LOD as low as 1.1 ng g^{-1} . Recent advances in Hg determination using solid sampling-electrothermal vaporization inductively coupled plasma mass spectrometry (SS-ETV-ICP-MS) were reported.^{32,33} On this aspect, an ETV coupled to ICP-MS was developed for ultra-trace Hg determination in bioresorbable calcium phosphate, offering an improved LOQ of $0.0002 \text{ } \mu\text{g g}^{-1}$, reduced sample preparation time, and low risk of contamination.^{32–34} In this context, the aim of this study is to develop an analytical method for Hg determination at ultra-trace levels in eye shadows using a new ETV system coupled to ICP-MS.

MATERIALS AND METHODS

Instrumentation

The ETV system used in this study has been detailed in previous reports.^{32,33,35} It comprises a halogen lamp (Osram, Germany, 650 W) housed in a custom-built glass chamber. The lamp has included a cavity that served as the sample holder. Positioned approximately 3 mm above this holder is a quartz tube (with an internal diameter of 2 mm), which extracts the vapor and minimizes Hg deposition on the vaporization chamber walls. The chamber is equipped with an input for argon, used as the carrier gas, and an output to direct the generated sample vapor toward the plasma. A solenoid valve (three-way, Cole-Parmer, USA) installed at the outlet of the vaporizer chamber allows the Ar gas to be directed from the vaporization chamber to the waste when the chamber is opened for the sample introduction and prevents plasma extinguishing. When the chamber is closed, the valve switches to direct the gas flow to the plasma. The vaporization chamber was connected to the plasma torch using a Tygon® tube. A proportional-integral (PI) control system and user interface were used to control the lamp heating time, temperature, and operation of the solenoid valve. It is worth highlighting that the temperature control of the ETV was implemented using a PI control system, which regulates the power supplied to the lamp by a power converter. The control system and the interface were developed using a commercial data acquisition system, LabVIEW environment (NI USB-6008, National Instruments, Austin, USA).

All measurements were performed using ICP-MS equipment (PerkinElmer Sciex, ELAN DRCII, Canada). The sensitivity evaluation and formation of oxides in the ICP-MS instrument were performed daily before the analysis. For this purpose, a solution containing $1 \text{ } \mu\text{g L}^{-1}$ of In and Ce was used, along with the ICP-MS in its standard configuration, by using a concentric nebulizer (Meinhard Associates, USA), a cyclonic spray chamber (Glass Expansion, Inc., Australia), radiofrequency power and plasma, auxiliary and nebulizer gas flow rates were 1300 W, 15.0, 1.2 and 1.00 L min^{-1} , respectively. The signal intensities of $^{115}\text{In}^+$, $^{140}\text{Ce}^+$, and $^{156}\text{CeO}^+$ were monitored to evaluate the sensitivity and oxide formation. The sensitivity values obtained were considered during data processing. Hg was also determined using a custom-built flow-injection cold vapor generation system coupled to ICP-MS (CV-ICP-MS). This system included a peristaltic pump (Ismatec, Switzerland), an injection valve with a $100 \text{ } \mu\text{L}$ sample volume, and a U-type gas-liquid separator. The ICP-MS operating conditions are described in Table I.

Table I. Instrumental parameters for Hg determination by SS-ETV-ICP-MS and CV-ICP-MS

Parameter	SS-ETV-ICP-MS	CV-ICP-MS
RF power (W)	1300	1300
Plasma gas flow rate (L min ⁻¹)	15.0	15.0
Auxiliary gas flow rate (L min ⁻¹)	2.0	2.0
Nebulizer/carrier gas flow rate (L min ⁻¹)	1.20	1.00
Dwell time (ms)	20	40
Sweeps per reading	1	1
Readings per replicate	150	750
Replicates	1	1
Isotope (<i>m/z</i> ratio)	²⁰² Hg	

To obtain reference results for Hg, sample digestion was carried out using a microwave-assisted wet digestion (MAWD) method with a Synthos 3000 microwave system (Anton Paar, Austria). The system was equipped with an HF100 rotor, which holds 16 modified polytetrafluoroethylene (PTFE-TFM) vessels, each with a 100 mL capacity (Anton Paar). The operational limit for this rotor was set at a maximum temperature of 220 °C, pressure of 40 bar, and microwave power of 1400 W.

Reagents and samples

Water used for standards and reagents preparation was purified through a Milli-Q system (Millipore, USA, 18.2 MΩ cm). Nitric acid (65%, 1.4 kg L⁻¹, Sigma Aldrich, USA) was distilled using a sub-boiling system (duoPUR, Milestone, Italy) and used for sample digestion and solution preparation. Hydrofluoric acid (40%, 1.15 kg L⁻¹, Sigma Aldrich) was used without further purification. Titanium oxide (Merck, Germany), quartz fiber membrane (Analytik Jena, Germany, order no. 402-889.039, adsorption material for boat combustion), and magnesium silicate (Merck) were tested for matrix adjustment with the aim of external calibration.

Mercury standard solutions were prepared by diluting a 1000 mg L⁻¹ stock solution (Merck) in 5% v/v HNO₃ for analysis by SS-ETV-ICP-MS and CV-ICP-MS. Solutions of 0.05% (m/v) NaBH₄ (Merck) prepared in NaOH (Merck), 0.01% m/v, and 1.0 mol L⁻¹ HCl (Vetec, Brazil) were used for Hg determination by CV-ICP-MS. Argon (99.996%, White Martins, Brazil) was used as the plasma gas and carrier gas.

Eye shadow samples were purchased locally and designated as Sample-1 (manufactured in Brazil), Sample-2 (manufactured in Brazil), and Sample-3 (manufactured in China). All samples were compact powders, with Sample-1 being green, Sample-2 brown, and Sample-3 black. Sample-1 was used for method optimization. Certified reference materials of Marine Sediment (MESS-3, National Research Council of Canada, NRC) and San Joaquin Soil (NIST 2709, National Institute of Standards and Technology, Gaithersburg, USA) were used for accuracy evaluation, as they predominantly comprise inorganic materials, with silicon and aluminum being the most abundant elements.

Microwave-assisted wet digestion

In order to obtain reference results for Hg, samples were digested by MAWD based on previous studies.²⁸ For this, an aliquot about 200 mg of the sample was weighed inside PTFE-TFM vessels, and 5 mL of 65% HNO₃ with 2 mL of 40% HF were added. The concentrated acid mixture was left to stand for 2 hours before being subjected to microwave heating, following the program: ramp of 10 min to 1400 W;

15 min at 1400 W; 20 min at 0 W (cooling). After cooling, the digested samples were diluted to 25 mL with ultrapure water for further analysis.

SS-ETV-ICP-MS procedure

For SS-ETV-ICP-MS analysis, the eye shadow samples were weighed directly onto small pieces of filter paper (2 x 3 cm) and then transferred to the sample hole of the lamp. The lamp, with the sample, was inserted into the vaporization chamber, followed by a 10 s purge to eliminate air from the system before initiating the heating program.³² Once the heating program was completed, the remaining sample residue was removed before starting a new program.

To optimize the SS-ETV-ICP-MS method, various parameters of the heating program, carrier gas flow rate, and sample mass were evaluated. Additionally, the most suitable calibration approach was assessed by comparing (i) external calibration with increasing the mass of CRM, (ii) external calibration with standard solutions, and (iii) external calibration with standard solutions in the presence of titanium oxide, magnesium silicate, or quartz fiber, for matrix matching or as support. After evaluating the calibration strategies, the samples were analyzed immediately after obtaining the calibration curve. Statistical analyses were conducted using the Student *t*-test and the ANOVA, *n* = 3, at a 95% confidence level (GraphPad InStat Software Inc., Version 3.06, USA, 2003).

RESULTS AND DISCUSSION

Optimization of ETV system conditions: heating program

The eye shadow samples, in the form of compact powders, predominantly consist of refractory compounds such as talc (60-80%), calcium or magnesium carbonate (5%), magnesium or zinc stearate (2-10%), pigments (2-30%), and kaolin (5-10%), which require high pyrolysis temperatures for efficient matrix removal.^{3,8,36,37} However, Hg has a low volatilization temperature, which can lead to analyte loss even under relatively low pyrolysis temperature conditions, such as 300 °C. In this context, the pyrolysis step can be omitted when the matrix is less volatile than the analyte. Thus, around 1.0 mg of the eye shadow sample (Sample-1) was subjected to a heating program based on the conditions of the literature.^{32,33} The program included a drying step at 80 °C for 20 s, vaporization at 650 °C for 10 s, and a final cooling step for 120 s.^{32,33} After that, the residue remaining on the sample holder was weighed to estimate the amount (*n* = 3), and over 95% of the sample remained on the sample holder. The amount of residue indicates that the matrix is refractory and has low volatility due to its mineral content.^{3,37,38} Refractory matrices containing volatile analytes minimize interference during analyte signal acquisition.^{32,33} Similarly, no interferences from the eye shadow were observed in determining Hg by the SS-ETV-ICP-MS method. Therefore, further experiments were performed without including the pyrolysis step.

To establish the heating program, only the vaporization step was evaluated, excluding the pyrolysis step, due to the higher volatility of the analyte relative to the matrix. The vaporization temperature was investigated for Sample-1 and the aqueous standard solution, given that calibration with a standard solution is more straightforward.³⁰ However, adding magnesium silicate to the standard solution was essential, as discussed in the *Analytical performances and eye shadow sample analysis* section. In addition, since the calibration was evaluated using the aqueous standard solution, the drying step (80 °C for 20 s) was used to ensure the removal of any residual moisture that could interfere with the vapor transport to the plasma. In this way, the same time and temperature program was applied to the solid samples. The vaporization temperature was optimized by monitoring the signal intensity over various temperatures, as shown in Figure 1.

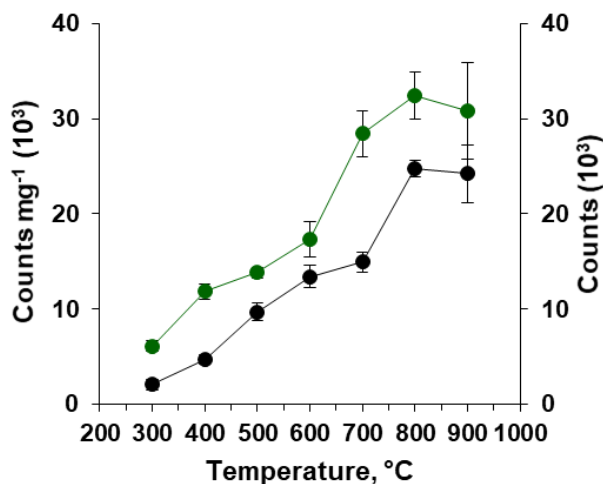


Figure 1. Vaporization temperatures for Hg: (●) axis on the left side represents the signal intensity normalized to 1.0 mg of Sample-1 and (●) on the right side represents the signal intensity for 2 μ L of aqueous standard solution (50 μ g of Hg) in the presence of magnesium silicate (2 mg). Conditions: 1.10 L min⁻¹ of carrier gas, drying step at 80 °C with a hold time of 20 s, and vaporization step with a hold time of only 10 s.

As observed in Figure 1, the signal intensity of Hg increases as the vaporization temperature increases, reaching a maximum between 700 and 900 °C for the sample. For the standard solution, the maximum intensity was observed between 800 and 900 °C. These results indicate that Hg vaporization is efficient within these temperature ranges, enabling calibration with the standard solution in the presence of magnesium silicate, thereby simplifying the analytical process. Beyond 800 °C, the signal intensities stabilize, suggesting no additional benefit in using higher temperatures. At 900 °C, the signal intensity has a relative standard deviation (RSD) of 23% for the sample and 13% for the standard solution. The worsening of precision (RSD) at 900 °C could be due to the proximity of this temperature to the maximum operational limit of the equipment, which may cause oscillations. This demonstrates that 800 °C is the most appropriate temperature for the quantitative complete vaporization of Hg, with an RSD below 8%. Therefore, based on these results, the vaporization temperature of 800 °C was selected for subsequent experiments, as it provided optimal vaporization efficiency for Hg in both the sample and the standard solution.

Optimization of ETV system conditions: carrier gas flow rate

The carrier gas flow rate is critical in ensuring effective analyte transport from the vaporization chamber to the ICP-MS instrument, minimizing analyte deposition within the chamber and along the transport line.³⁰ Accordingly, the influence of carrier gas flow rate was evaluated from 0.90 to 1.30 L min⁻¹ to determine the condition optimal flow rate that maximizes Hg signal intensity while maintaining good precision. This assessment included Hg intensities for Sample-1 and the standard solution in the presence of 2 mg of magnesium silicate in response to variations in argon flow rate (Figure 2).

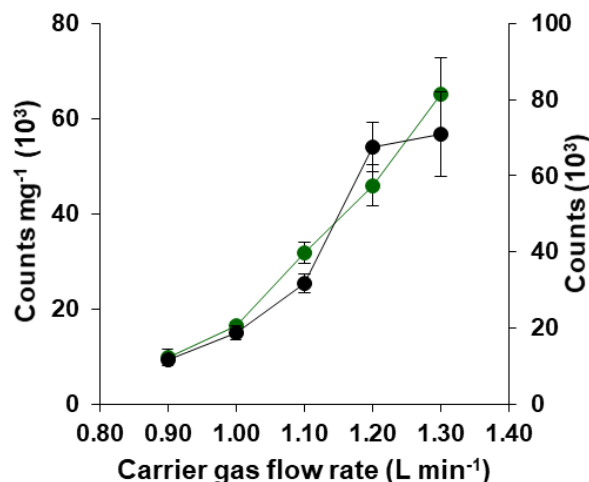


Figure 2. Effect of carrier gas flow rate on Hg signal intensity: (●) axis on the left side represents the signal intensity normalized to 1.0 mg of Sample-1 and (●) on the right side represents the signal intensity for 2 μ L of standard solution (50 pg of Hg) in the presence of magnesium silicate (2 mg). Conditions: drying step at 80 °C with a hold time of 20 s, vaporization at 800 °C with a hold time of 10 s.

The Hg signal intensity increased as the gas flow rate increased for the sample and the standard solution, reaching a maximum of 1.30 L min⁻¹. However, at flow rates between 1.20 and 1.30 L min⁻¹, a relative standard deviation (RSD) ranging from 11% to 17% was observed, worsening signal stability. These elevated RSD values can be attributed to fluctuations in the characteristics of the analytical plasma zone, such as electron density, temperature, and the concentration of analyte-reactive species.³⁹ Consequently, a carrier gas flow rate of 1.10 L min⁻¹ was selected as the most suitable, offering the optimal compromise between high signal intensity and precision (RSD lower than 8%) for both the sample and the standard solution.

Optimization of ETV system conditions: sample mass

The sample mass introduced into the plasma by the ETV system is a critical parameter for ensuring precise and accurate results. The sample amount, concomitant elements, and the matrix can enhance or suppress the analytical signal of specific elements, mainly due to transport and thermal effects on the ETV system and alterations in plasma characteristics.^{30,39,40} In this study, the evaluation was performed by plotting the signal intensity as a function of sample mass introduced into the vaporization chamber within the linear response range of Hg. Sample masses tested ranged from 0.2 to 5 mg under previously optimized operational conditions. Individual signal intensity measurements were compiled into discrete mass intervals, and the mean Hg signal intensities corresponding to these intervals were calculated, as shown in Figure 3. The mean signal intensities for each interval were statistically analyzed using ANOVA (95% confidence level). The results indicated that Hg determination can be done with eye shadow samples ranging from 0.2 mg to 4 mg without significant differences in response. Therefore, sample masses up to 4 mg can be used without interferences, contributing to a low LOQ for the method.

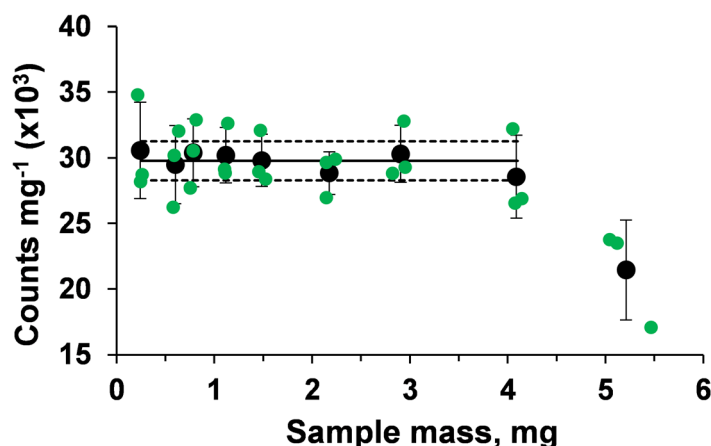


Figure 3. Effect of sample mass on Hg signal intensity. (●) Individual result of Hg intensity for each sample mass. (●) Results of the mean Hg intensity for each sample mass range. (—) The result of the mean Hg intensity was obtained from the suitable mass range for the analysis. Conditions: Sample-1, to 1.10 L min⁻¹ of carrier gas, drying step at 80 °C with a hold time of 20 s, and vaporization at 800 °C with a hold time of 10 s.

Analytical performances and eye shadow sample analysis

The CRM MESS-3, Marine Sediment, was used in increasing quantities for calibration evaluation. This study achieved calibration within 20 to 100 pg of Hg, with a satisfactory correlation coefficient (R^2) of 0.9898 (Figure 4). However, some limitations were observed using external calibration with CRM, such as CRMs with a matrix similar to the sample and a CRM mass that matched the analyte concentration range present in the samples. For the CRM used in this study, the calibration range was 20 to 100 pg Hg, with the lowest mass of Hg set at 20 pg due to the difficulty of weighing masses below 0.2 mg. Another limitation involves reproducing the blank in direct solid sample analysis. After submitting the CRM to a vaporization step, the residue was used to simulate a blank. All analysis steps were simulated, including weighing, transferring to the sample holder, and introducing it into the vaporization chamber, followed by the vaporization and Hg measurement. In addition, the high cost of CRM represents a drawback for its routine application.

In this context, external calibration with a standard solution evaluated an alternative calibration strategy. Five mono elemental Hg standard solutions were prepared in 5% v/v HNO₃, where 2 µL were pipetted onto the sample holder of the vaporization chamber. The calibration curve did not exhibit satisfactory linearity or repeatability during the initial calibration using only the standard solution. Therefore, calibration was evaluated with a standard solution combined with titanium oxide or magnesium silicate, as previous studies suggest that analyte transport efficiency increases in solid samples and suspensions compared to solution calibration.^{30,40,41} Magnesium silicate and titanium oxide were selected due to their presence in the eye shadow samples, representing about 60% of the mineral content.^{3,38}

In the first test, 2 µL of the standard solution was dispensed onto 2 mg of titanium oxide and then submitted to the heating program. After each heating program, the residue was removed, and other aliquots of the standard solution and titanium oxide were introduced. With titanium oxide, more than 95% remained on the holder after heating. However, the residue became compact and adhered to the sample holder, making its removal difficult and reducing the practicality of this calibration approach. In contrast, calibration using a standard solution in the presence of 2 mg of magnesium silicate shows to be more suitable. The residue of the magnesium silicate was quickly removed from the holder after the heating program. After heating, more than 95% of the magnesium silicate remained on the holder and was removed by inverting the sample holder.

External calibration using a standard solution and magnesium silicate resulted in good linearity, with a correlation coefficient (R^2) of 0.9983, allowing SS-ETV-ICP-MS calibration within the range of 5 to 100 pg of Hg, as presented in Figure 4B. The RSD for all Hg masses used for the calibration curve was below 7%, demonstrating the high repeatability of this calibration method. Another alternative calibration approach studied involved applying the standard solution to a quartz fiber instead of magnesium silicate. However, no linearity was achieved in the calibration curve, and the quartz fiber remained in the sample holder. Therefore, magnesium silicate is the most suitable material for matching the sample matrix. In addition, it acts as a modifier and enhances analyte transport, improving the analyte transfer to the ICP-MS, improving sensitivity and LOQ.^{30,40,41}

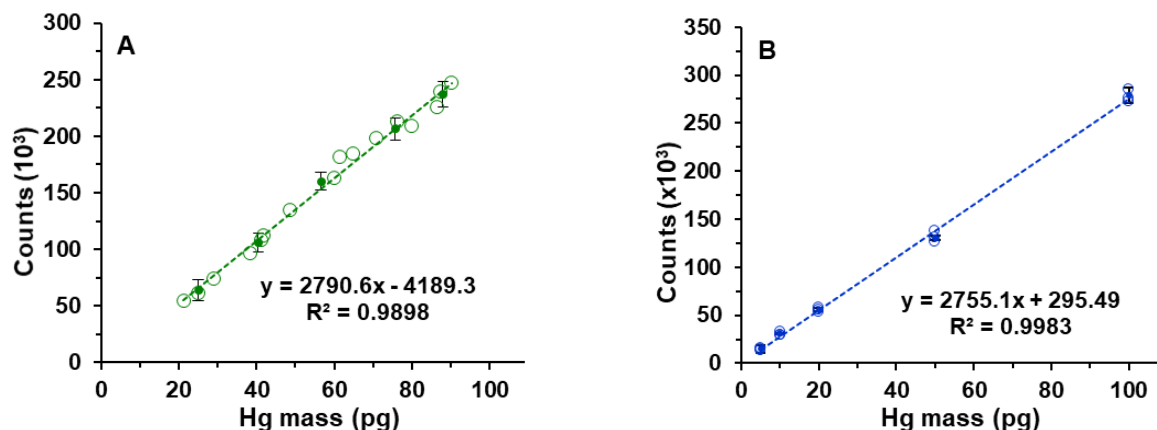


Figure 4. (A) External calibration with CRM and (B) external calibration with standard solutions (2 μ L) in the presence of 2 mg of magnesium silicate. Conditions: 1.10 L min^{-1} of carrier gas, drying step at 80 $^{\circ}\text{C}$ with a hold time of 20 s, and vaporization at 800 $^{\circ}\text{C}$ with a hold time of 10 s.

To evaluate the analytical signal profile from matrices used in the optimization of the method, an aliquot of 0.504 mg of MESS-3, a standard solution containing 25 pg of Hg pipetted onto 2 mg of magnesium silicate, 1.038 mg of eye shadow, and the residue remaining after the heating program were analyzed under optimized conditions (Figure 5). As observed, the transient signal profiles for Hg differed among the sample, CRM, and standard solution in the presence of magnesium silicate, indicating matrix-dependent vaporization behavior. These differences in quantification were compensated by using signal integration, as demonstrated by the statistically equivalent calibration curves presented in Figure 4. More details about the matrix effect, mainly related to Mg and the CRM, were not conducted in this study. An analysis of variance (ANOVA) test was performed to compare the two regression models (Figures 4A and 4B), and the results showed no significant differences between the models (ANOVA, 95% confidence level). These results demonstrate the feasibility of using external calibration with a standard solution for Hg determination in eye shadow samples, minimizing the dependence on CRM calibration. Moreover, the Hg signal intensity from the sample residue was negligible, indicating that the analyte was quantitatively volatilized from the matrix using the SS-ETV-ICP-MS method.

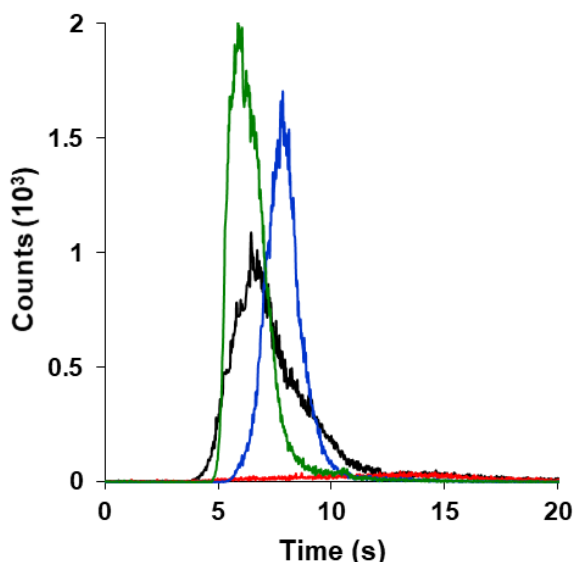


Figure 5. Signal profiles of Hg obtained by SS-ETV-ICP-MS for (—) 1.038 mg of Sample-1, (—) Sample-1 residue, (—) 0.504 mg of MESS-3, and (—) 2 μ L of standard solution (25 μ g of Hg) deposited on 2 mg of magnesium silicate. Conditions: 1.10 L min^{-1} of carrier gas, drying step at 80 $^{\circ}\text{C}$ with a hold time of 20 s, and vaporization at 800 $^{\circ}\text{C}$ with a hold time of 10 s.

Therefore, external calibration using a standard solution in the presence of magnesium silicate demonstrated better performance than calibration using CRM. In this context, the solid sampling method using SS-ETV-ICP-MS was applied to analyze eye shadow samples, and the results obtained with external calibration using standard solution are listed in Table II. The results for the samples NIST 2709 and MESS-3 did not present significant differences compared to certified values (t -test, 95% confidence level). Although the precision of Hg results for the samples and CRMs showed an RSD of 6 to 11%, this is considered acceptable. In general, the precision of results obtained by direct solid analysis, specifically ETV, is around 15%.^{30,40} Table II also presents the results for the samples obtained by CV-ICP-MS after microwave-assisted digestion, in which the values are below the LOQ.

Table II. Results obtained for Hg in eye shadow samples and CRMs by SS-ETV-ICP-MS using standard solution calibration and CV-ICP-MS after acid digestion. Mean \pm standard deviation ($\mu\text{g g}^{-1}$) for $n = 3$.

Sample ($\mu\text{g g}^{-1}$)	SS-ETV-ICP-MS	CV-ICP-MS
Sample-1	0.056 ± 0.005	$< 0.1^a$
Sample-2	0.082 ± 0.006	$< 0.1^a$
Sample-3	0.047 ± 0.003	$< 0.1^a$
NIST 2709 ^b	1.42 ± 0.15	nd ^d
MESS-3 ^c	0.094 ± 0.009	nd ^d
LOQ ($\mu\text{g g}^{-1}$)	0.001	0.1

^a LOQ using the CV-ICP-MS reference method

^b NIST 2709, San Joaquin Soil, certified value: $1.40 \pm 0.08 \mu\text{g g}^{-1}$

^c MESS-3, Marine Sediment, certified value: $0.091 \pm 0.009 \mu\text{g g}^{-1}$

^d nd: not determined

Under the optimized ETV heating program and the operating parameters of the SS-ETV-ICP-MS, the analytical performance for Hg determination was evaluated. The LOQ was calculated based on the 10σ criterion, $LOQ = 10 \times \sigma$, where the standard deviation (σ) was obtained from 10 measurements of the blank solution, pipetted onto 2 mg of magnesium silicate. In addition, the maximum sample mass (4 mg) that the SS-ETV-ICP-MS can analyze was used. The LOQ of the SS-ETV-ICP-MS method with calibration using standard solution is listed in Table II, allowing for comparison with the results obtained by the CV-ICP-MS method. It was observed that the SS-ETV-ICP-MS method using standard solution calibration in the presence of magnesium silicate provided a low LOQ and is a more straightforward approach than CV-ICP-MS method. Since the determination of Hg by CV-ICP-MS requires a sample preparation step involving MAWD, using a concentrated mixture of 5 mL of 65% HNO_3 with 2 mL of 40% HF, and even with a relatively high sample mass (200 mg), the LOQ was higher than that of the SS-ETV-ICP-MS. Furthermore, the CV-ICP-MS needs at least a ten-fold dilution step to minimize interference during Hg determination and to reduce the risk of damaging the ICP-MS interface due to the high acid content, particularly HF.

CONCLUSIONS

A solid sampling method using ETV-ICP-MS was developed to determine Hg at low concentrations in eye shadow. Under optimized conditions, it was possible to implement a practical external calibration strategy using a standard solution in the presence of magnesium silicate. This approach resulted in good linearity of the calibration curve and enhanced analyte transport efficiency, attributed to the improved transfer of Hg to the plasma facilitated by the magnesium silicate particles formed during vaporization. Moreover, the SS-ETV-ICP-MS method with external calibration using the standard solution provided a lower LOQ than CV-ICP-MS after acid digestion of the sample. Another advantage of this method is the possibility of quantifying Hg without a pyrolysis step, which reduces analysis time and minimizes the risk of analyte loss due to volatilization. The method also proved effective for analyzing small amounts of eye shadow without compromising the LOQ.

Conflicts of interest

The authors confirm that they have no conflicts of interest.

Acknowledgements

The authors are grateful to FAPERGS (grant number 24/2551-0001566-3) and CNPq for supporting this study.

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