



# Effect of different precursors on generation of reference spectra for structural molecular background correction by solid sampling high-resolution continuum source graphite furnace atomic absorption spectrometry: Determination of antimony in cosmetics

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## ABSTRACT

Different precursors were evaluated for the generation of reference spectra and correction of the background caused by SiO molecules in the determination of Sb in facial cosmetics by high-resolution continuum source graphite furnace atomic absorption spectrometry employing direct solid sample analysis. Zeolite and mica were the most effective precursors for background correction during Sb determination using the 217.581 nm and 231.147 nm lines. Full  $2^3$  factorial design and central composite design were used to optimize the atomizer temperature program. The optimum pyrolysis and atomization temperatures were 1500 and 2100 °C, respectively. A  $\text{Pd}(\text{NO}_3)_2/\text{Mg}(\text{NO}_3)_2$  mixture was employed as the chemical modifier, and calibration was performed at 217.581 nm with aqueous standards containing Sb in the range 0.5–2.25 ng, resulting in a correlation coefficient of 0.9995 and a slope of  $0.1548 \text{ s ng}^{-1}$ . The sample mass was in the range 0.15–0.25 mg. The accuracy of the method was determined by analysis of Montana Soil (II) certified reference material, together with addition/recovery tests. The Sb concentration found was in agreement with the certified value, at a 95% confidence level (paired *t*-test). Recoveries of Sb added to the samples were in the range 82–108%. The limit of quantification was  $0.9 \text{ mg kg}^{-1}$  and the relative standard deviation ( $n=3$ ) ranged from 0.5% to 7.1%. From thirteen analyzed samples, Sb was not detected in ten samples (blush, eye shadow and compact powder); three samples (two blush and one eye shadow) presented Sb concentration in the  $9.1 - 14.5 \text{ mg kg}^{-1}$  range.

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## 1. Introduction

Despite the fact that hazardous metals are not acceptable in cosmetics, antimony-containing compounds may be present as pigments to give red, yellow, or blue colors to facial makeup products [1]. Antimony and its compounds can cause a number of human health effects, including respiratory and gastrointestinal diseases and contact dermatitis [1,2]. German and Canadian regulatory agencies have established a concentration of  $10 \text{ mg kg}^{-1}$  as the maximum acceptable level of Sb in cosmetics [3,4]. Hence, appropriate methods for the determination of toxic metals in makeup products are needed in order to ensure product quality and the safety of cosmetics for users worldwide.

The major components commonly present in the composition of facial makeup (including alumina, silica, titanium dioxide, mica,

and inorganic pigments) are refractory, which makes analysis difficult. The presence of these refractory components necessitates extreme conditions for the dissolution of makeup to give a clear solution, and conventional procedures are based on dry ashing or wet digestion [5–7]. Disadvantages of these techniques are that they are laborious, time consuming, and susceptible to contamination and analyte losses. They also involve high energy consumption, the use of large quantities of hazardous chemical reagents, and the generation of substantial amounts of waste. As an alternative, direct solid sample (DSS) analysis is an environmentally friendly method that avoids the lengthy pretreatments associated with conventional analysis of makeup samples [8,9].

Among *spectrometric techniques for elemental analysis*, high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) hyphenated with SS is a versatile technique that offers several advantages. Solid samples can be measured directly without any previous treatment, sample throughput can be greatly increased, waste generation is low, and

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the method is relatively inexpensive. The technique enables elimination of the fine structured background caused by diatomic molecular species, using a least-squares background correction (LSBC) algorithm [10,11]. Nevertheless, the efficacy of LSBC depends on correct selection of the precursor used to generate a reference spectrum representing the structured molecular background of the sample matrix [12,13]. In GFAAS, blanks, standards, and samples are analyzed using the same atomizer heating program, but the molecular background reference spectrum, which is typically generated from pure substances or mixtures, may not be entirely similar to the spectra of real samples. Concomitants present in the sample matrix can affect the kinetics of formation of diatomic molecules, hence altering the background absorption profile [12]. Therefore, the identification and use of suitable precursors in HR-CS SS-GF AAS is not as straightforward as one might think.

The determination of Sb by HR-CS SS-GF AAS has been described for dust [14], airborne particulate matter [15], and sediment [16] matrices. All these complex samples contain Si as a major concomitant, but structured SiO backgrounds have only been reported for determination of Sb using the lines at 212.739 and 231.147 nm, with Ru [15] and Ir [16] as permanent modifiers, respectively. The interferences caused by SiO and PO in the determination of Sb in sediment were eliminated when the LSBC employed the combined molecular background reference spectra for pure SiO<sub>2</sub> and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> [16]. Preliminary tests in our laboratories showed that the use of SiO<sub>2</sub> alone was inadequate for pre-recording a suitable structured SiO background to be used as the reference spectrum in determination of Sb in makeup by HR-CS SS-GF AAS.

Considering the above, this paper describes the evaluation of different precursors used to generate SiO background reference spectra, in order to develop a simple and accurate method for Sb determination in facial makeup samples by HR-CS SS-GF AAS.

## 2. Material and methods

### 2.1. Instrumentation

An Analytik Jena contrAA 700 high-resolution continuum source atomic absorption spectrometer equipped with a xenon short-arc lamp (XBO 301, 300 W, GLE, Berlin, Germany) as a continuum radiation source was used throughout this work. The spectrometer was fitted with a compact high-resolution monochromator, comprising a prism and an Echelle grating with a spectral bandwidth of less than 2 pm per pixel in the far ultraviolet range, together with a charge-coupled device (CCD) array detector. Atomization was performed using pyrolytic carbon-coated graphite tubes (without a dosing hole) and graphite platforms. The samples were weighed directly onto the platforms using a micro-balance (WZ2PW, Sartorius Göttingen, Germany) with precision of 0.001 mg, and were introduced into the atomization compartment using an Analytik Jena SSA 600 automated solid sampling accessory. High purity argon (99.996%, White Martins, São Paulo, Brazil) was used as the purge and protective gas.

### 2.2. Reagents, analytical solutions, and samples

The high purity water (resistivity 18.2 MΩ cm) used to prepare all the solutions was obtained from a Millipore Rios 5<sup>®</sup> reverse osmosis system coupled to a Milli-Q Academic deionizer (Millipore, Bedford, MA, USA).

Standard solutions containing 250 and 600 µg L<sup>-1</sup> Sb were prepared daily by appropriate dilution of the 1000 mg L<sup>-1</sup> Sb stock

solution (Titrisol<sup>®</sup>, Merck) in 0.1% (v/v) Suprapur HNO<sub>3</sub> (Merck, Darmstadt, Germany). Different aliquots of 250 and 600 µg L<sup>-1</sup> standard solutions were injected onto the platforms for calibrations using the Sb lines at 217.581 nm (0.5, 0.75, 1.0, 1.25, 1.5, and 2.0 ng Sb) and 231.147 nm (1.2, 2.4, 3.6 and 4.8 ng Sb), respectively.

A modifier solution containing 1000 mg L<sup>-1</sup> Pd(NO<sub>3</sub>)<sub>2</sub> plus 500 mg L<sup>-1</sup> Mg(NO<sub>3</sub>)<sub>2</sub> was prepared by the appropriate dilution of 10 g L<sup>-1</sup> Pd(NO<sub>3</sub>)<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub> stock solutions (Merck, Darmstadt, Germany) in 0.05% (m/v) Triton X-100 (Mallinckrodt Baker, Paris, KY, USA).

Different precursors were evaluated for generation of the SiO<sub>(g)</sub> structured background: SiO<sub>2</sub> (99%, 0.5–10 µm, Sigma-Aldrich, USA); TiO<sub>2</sub> (99.8%, Sigma-Aldrich, USA); Mica Covasil 4.05 (K<sub>2</sub>O · 3Al<sub>2</sub>O<sub>3</sub> · 6SiO<sub>2</sub>, Sensient Cosmetic Technologies, France); and CBV100 Zeolite Y (Na form, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=5, Zeolyst International, USA).

Eye shadow, blush, and compact powder samples of various brands and in diverse colors were purchased locally in the city of Araraquara (São Paulo, Brazil). Makeup reference materials are unavailable, so the Montana Soil (II) certified reference material (CRM NIST 2711a) (Gaithersburg, MD, USA) was selected for the evaluation of accuracy, since the major components of its matrix are similar to those present in the composition of makeup.

All plastic bottles and glassware materials were cleaned by soaking in 10% (v/v) HNO<sub>3</sub> for at least 24 h. Before use, these materials were rinsed abundantly with deionized water.

### 2.3. Effect of precursors on background correction

Preliminary tests showed that the Sb line at 217.581 nm was within the range of strong molecular absorption bands with significant fine structure, attributed to SiO, which needed to be corrected in order to avoid interferences. The feasibility of generating SiO molecular reference spectra suitable for background correction in the determination of Sb in cosmetics was evaluated using the following precursors: SiO<sub>2</sub>; mixture of SiO<sub>2</sub> and TiO<sub>2</sub> oxides with mass ratios of 1:1, 1:2, 1:3, 1:4, and 1:5; mica; and zeolite. These studies were carried out using a preliminary heating program under the conditions described elsewhere [16,17]. The optimum precursor obtained was then employed in further studies.

### 2.4. Optimization of the atomizer heating program

An eye shadow sample was selected to optimize the main parameters of the atomizer heating program for Sb determinations by HR-CS SS-GF AAS in the presence of the 5.0 µg Pd(NO<sub>3</sub>)<sub>2</sub> + 2.5 µg Mg(NO<sub>3</sub>)<sub>2</sub> as the chemical modifier. This optimization was performed using a full (2<sup>3</sup>) factorial design, considering the following factors: pyrolysis temperature, atomization temperature, and sample size. Considering these factors at high and low levels, coded as +(1600 °C pyrolysis temperature; 2200 °C atomization temperature; 0.45–0.55 mg sample mass) and –(1400 °C pyrolysis temperature; 2000 °C atomization temperature; 0.15–0.25 mg sample mass), respectively, eight experiments were designed and performed in triplicate, as detailed in Table S1.

The response monitored in these experiments was the normalized integrated absorbance at 217.581 nm, corrected for the background. The experiments were performed in random order to avoid systematic errors, and the experimental data were processed using Statgraphics Centurion XVI (v.16.1.15) software.

It was found that the pyrolysis and atomization temperatures significantly influenced the normalized integrated absorbance, so a new experimental design was carried out to provide a better evaluation of these factors. A central composite design (CCD) was used, considering the following coded levels: high (+) (1600 °C pyrolysis temperature; 2200 °C atomization temperature), low (–)

(1400 °C pyrolysis temperature; 2000 °C atomization temperature), central (0) (1500 °C pyrolysis temperature; 2100 °C atomization temperature),  $+\sqrt{2}$  (1640 °C pyrolysis temperature; 2240 °C atomization temperature) and  $-\sqrt{2}$  (1360 °C pyrolysis temperature; 1960 °C atomization temperature). The corresponding values of the levels of the factors and their combination are shown in Table S2.

The experiments were performed in random order to avoid systematic errors, and the response monitored was the normalized integrated absorbance at 217.581 nm, corrected for the background. The Statgraphics Centurion XVI (v.16.1.15) software was used for data processing.

## 2.5. Analytical procedure

The possibility of using aqueous standards calibration for direct solid sample analysis was evaluated by means of multiple effects matrices, comparing the characteristic masses ( $m_0$ ) and the slopes of the analytical curves (in the 0–4.8 ng mass range) constructed for the standards in (i) 0.1% (v/v) HNO<sub>3</sub> and (ii) the soil CRM.

Accuracy was assessed by analyzing the soil CRM, and comparing the found and certified values using the unpaired *t*-test. The Sb line at 231.147 nm (34% relative sensitivity) was used because the certified Sb value of the CRM ( $24.38 \pm 1.66$  mg kg<sup>-1</sup>) was higher than the upper limit of the linear response established for the line at 217.581 nm. It is worth highlighting that the structured background observed for the line at 231.147 nm was efficiently corrected by LSBC using the reference spectrum from zeolite.

Accuracy was also evaluated by means of addition/recovery tests. Eye shadow, blush, compact powder, zeolite, and mica samples (0.2 mg) were spiked with 5.0 and 7.0 µL aliquots of 250 µg L<sup>-1</sup> stock standard solution in order to obtain final concentrations of 6.2 and 8.7 mg kg<sup>-1</sup>, respectively. The spiked samples were transferred to the solid sample platform for analysis.

The precision of the method was evaluated in terms of the relative standard deviation (RSD) obtained for three successive measurements of each sample.

The limits of detection (LOD) and quantification (LOQ) were determined according to the IUPAC recommendations [18]:  $3 \times SD^{\text{blank}}/b$  (LOD), and  $10 \times SD^{\text{blank}}/b$  (LOQ), where SD is the standard deviation for ten blank measurements (using an empty platform) and *b* is the angular coefficient of the calibration curve.

After optimizing the calibration conditions, the method was applied in determination of Sb in commercial makeup samples. Aliquots of aqueous standards were manually injected on to the SSA 600 platform using micropipettes. Sample masses in the range 0.15–0.25 mg were manually transferred to the graphite platforms, weighed, and introduced into the atomization compartment using the automated solid sampling accessory. Atomic absorption measurements were carried out at 217.581 and 231.147 nm for the samples and the CRM, respectively. The optimized graphite tube heating program is provided in Table 1. For the purposes of

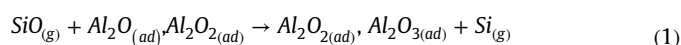
comparison, the integrated absorbance values obtained with DSS were normalized to 1.0 mg of sample. All measurements were carried out in triplicate (*n*=3), and the integrated absorbance was equivalent to 3 pixels.

## 3. Results and discussion

### 3.1. Evaluation of different precursors for background correction

Preliminary experiments revealed a pronounced effect of spectral interference from the structured background on the determination of Sb in facial cosmetics and the CRM. These interferences were attributed to strong SiO absorption bands that overlapped with the Sb line at 217.581 and 231.147 nm. These interferences could be corrected automatically by the LSBC algorithm available in the HR-CS GFAAS software, using a spectrum representing the sample background as a reference. To this end, different precursors were evaluated for the generation of a spectrum with a profile close to the structural molecular background of the sample spectra. The correction procedure adopted here began with the acquisition of a spectrum for the following precursors: 0.2 mg zeolite, 0.2 mg mica, 0.2 mg SiO<sub>2</sub>, 0.1 mg SiO<sub>2</sub> + 0.1 mg TiO<sub>2</sub>, 0.1 mg SiO<sub>2</sub> + 0.2 mg TiO<sub>2</sub>, 0.1 mg SiO<sub>2</sub> + 0.3 mg TiO<sub>2</sub>, 0.1 mg SiO<sub>2</sub> + 0.4 mg TiO<sub>2</sub>, and 0.1 mg SiO<sub>2</sub> + 0.5 mg TiO<sub>2</sub>.

The background of the makeup samples was attributed essentially to SiO, so the first experiments were focused on generation of a background from SiO<sub>2(s)</sub> alone. Fig. 1 shows time-resolved absorbance spectrum for Sb at 217.581 nm for an eye shadow sample, without correction (Fig. 1a) and after LSBC (Fig. 1c). It can be seen that the profiles of the SiO background generated from SiO<sub>2(s)</sub> and the sample were different, suggesting a substantial influence of the sample matrix on generation of SiO<sub>(g)</sub>. An attempt was therefore made to determine the influence of matrix effects on the background structure. A facial cosmetic such as eye shadow contains around 5% TiO<sub>2</sub> and 56% mica (KAl<sub>2</sub>Si<sub>3</sub>AlO<sub>10</sub>(OH,F)<sub>2</sub>) [19]. In order to evaluate the influence of sample composition on the SiO background structure, reference spectra were obtained from the SiO<sub>2</sub>:TiO<sub>2</sub> mixtures at different ratios (1:1, 1:2, 1:3, 1:4, and 1:5 w/w) and from the mica and zeolite samples. Zeolite was used here because, like mica, it is an aluminum silicate. Fig. S1 shows the temporal profiles of the SiO backgrounds generated from SiO<sub>2(s)</sub>, the eye shadow sample, and the SiO<sub>2</sub>/TiO<sub>2</sub> mixtures. It can be seen that the maximum transient absorbance of SiO<sub>(g)</sub> generated from SiO<sub>2</sub> appeared faster than obtained using the sample. As the TiO<sub>2</sub> in the mixture increased, the corresponding transient signals became longer. The times for the SiO<sub>(g)</sub> peak maxima were closely similar for the sample and SiO<sub>2</sub>:TiO<sub>2</sub> at a ratio of 1:3 (w/w). A delay in the time for formation of SiO<sub>(g)</sub> was observed when zeolite and mica were used as precursors (Fig. S2). It is likely that the constituents TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> acted as chemical modifiers, delaying the formation of SiO<sub>(g)</sub>. According to the literature, the thermal decomposition of Al<sub>2</sub>O<sub>3(s)</sub> begins before the decomposition of SiO<sub>2(s)</sub>, since energies of 501.6 and 799.6 kJ mol<sup>-1</sup> are required to dissociate the Al-O and Si-O bonds, respectively. The thermal decomposition products of Al<sub>2</sub>O<sub>3</sub> (such as Al<sub>2</sub>O<sub>2(g)</sub>, Al<sub>2</sub>O<sub>(g)</sub>, and Al<sub>(g)</sub>) are oxidized to Al<sub>2</sub>O<sub>3(ad)</sub>, Al<sub>2</sub>O<sub>2(ad)</sub>, and Al<sub>2</sub>O<sub>(ad)</sub> due to the presence of the Mg(NO<sub>3</sub>)<sub>2</sub> modifier [20,21], and may react with SiO<sub>(g)</sub> to produce Si<sub>(g)</sub> (Eq. 1). The Si<sub>(g)</sub> can then be oxidized to SiO<sub>(g)</sub> by oxygen. Hence, the time required for formation of SiO<sub>(g)</sub> from SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is longer than observed in the presence of SiO<sub>2(s)</sub> alone. The TiO<sub>2</sub> present in the mixed precursor may act similarly to Al<sub>2</sub>O<sub>3</sub>, increasing formation of the target SiO<sub>(g)</sub> molecule.

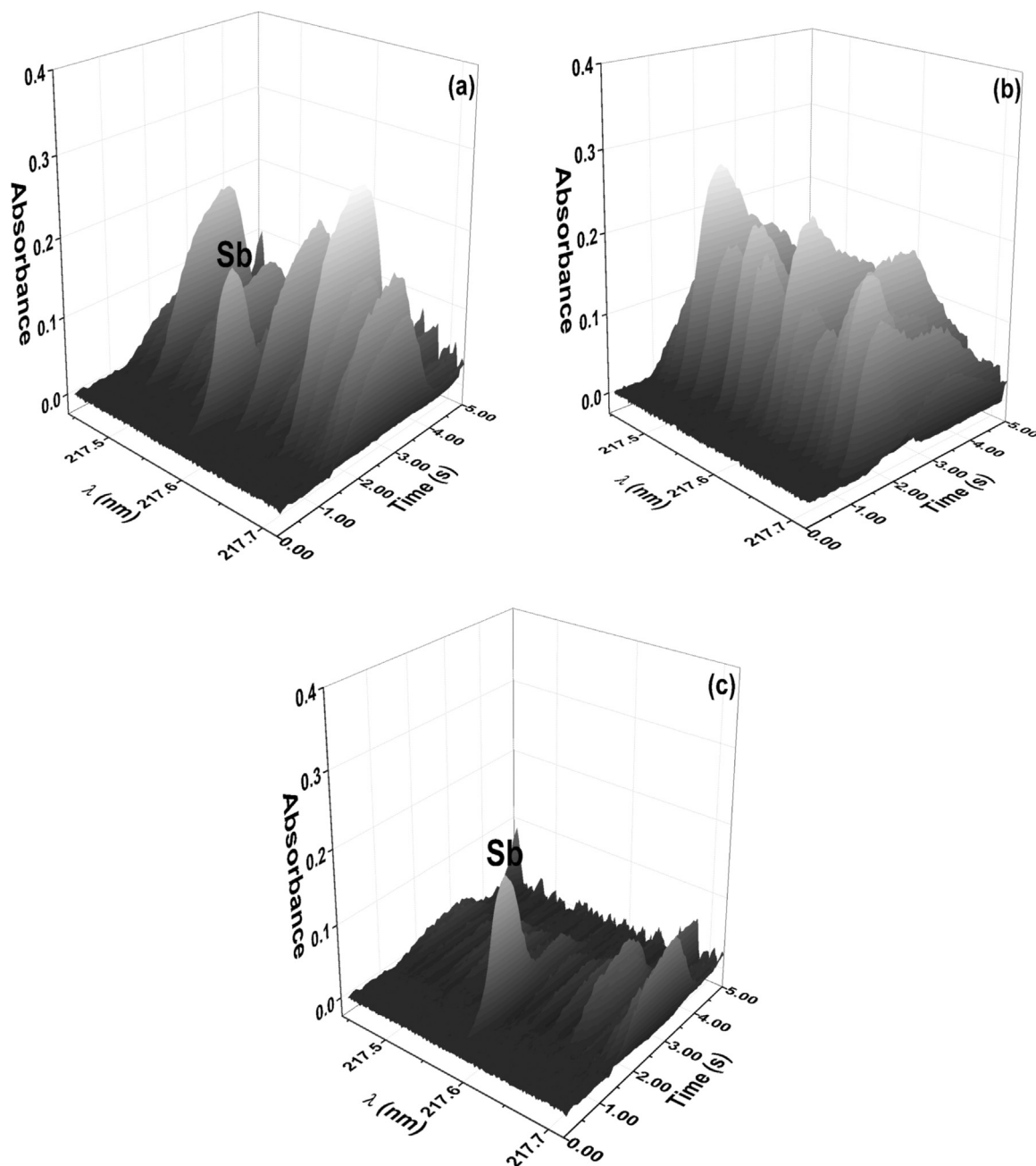


**Table 1**

Optimized heating program for determination of Sb in eye shadow, blush, and compact powder samples.

Step	Temperature (°C)	Ramp (°C s <sup>-1</sup> )	Hold time (s)	Argon flow rate (L min <sup>-1</sup> )
Drying 1	110	10	10	2.0
Drying 2	130	5	10	2.0
Pyrolysis	1500	50	30	2.0
Auto-zero <sup>a</sup>	1500	0	5	0
Atomization	2100	2100	5	0
Cleaning	2650	500	5	2.0

<sup>a</sup> Step to ensure that the atomization starts without the presence of argon.



**Fig. 1.** Time-resolved absorbance spectrum, in the vicinity of the 217.581 nm Sb line, for (a) eye shadow sample ( $9.1 \pm 0.9 \text{ mg kg}^{-1}$ ) without correction, (b) SiO generated from SiO<sub>2</sub>, and (c) eye shadow sample ( $9.1 \pm 0.1 \text{ mg kg}^{-1}$ ) after correction with LSBC.

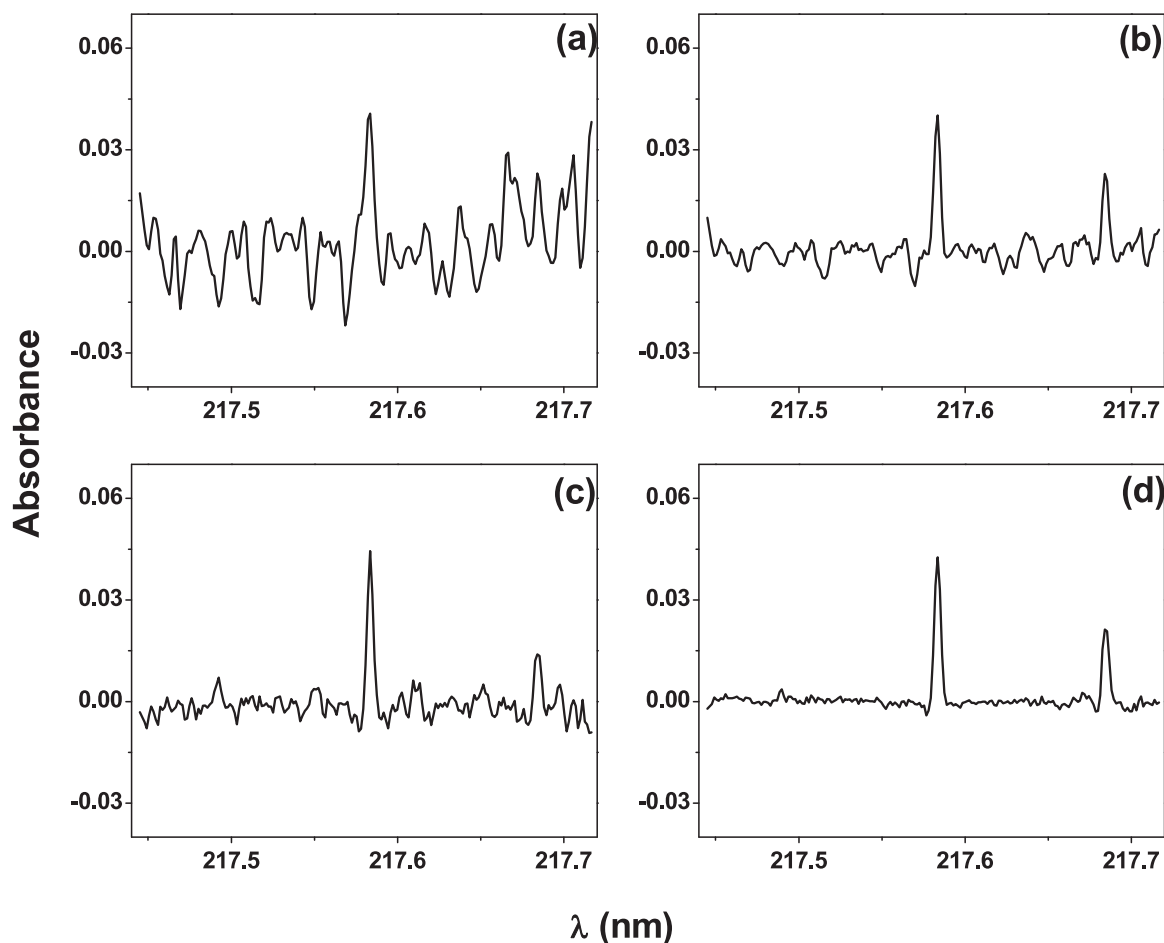
Fig. S3 shows the SiO spectra generated from the following precursors: eye shadow sample, SiO<sub>2</sub>, SiO<sub>2</sub>/TiO<sub>2</sub>, mica, and zeolite. Similar SiO<sub>(g)</sub> band profiles were obtained in the spectra for the sample, SiO<sub>2</sub>/TiO<sub>2</sub>, mica, and zeolite. Subsequently, LSBC was applied to the measurements of Sb in one eye shadow sample, using the reference spectra generated from SiO<sub>2</sub>, SiO<sub>2</sub>/TiO<sub>2</sub>, mica, and zeolite (Fig. 2). Use of the zeolite spectrum resulted in the best atomic absorption spectrum for Sb in the eye shadow sample, so zeolite was selected as the precursor in subsequent studies.

### 3.2. Optimization of pyrolysis and atomization temperatures and sample size

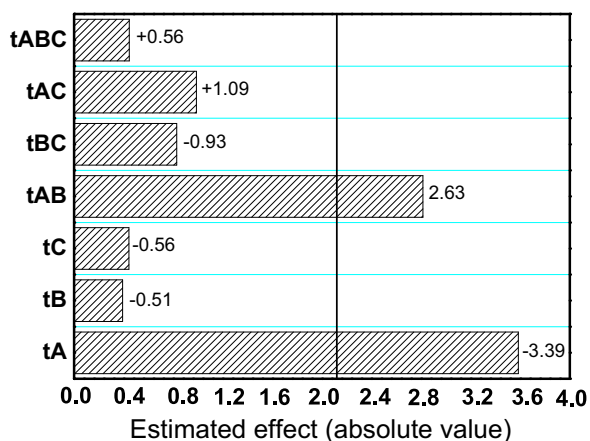
The pyrolysis temperature, atomization temperature, and sample size are the factors that have the greatest influence in absorbance measurements by HR-CS SS-GF AAS, and were firstly

evaluated at two levels using a full  $2^3$  factorial design. For each experimental condition, the integrated absorbance was measured, normalized, and corrected by LSBC using the zeolite reference spectrum. The experimental conditions and the corresponding responses (normalized integrated absorbance) were submitted to statistical analysis to estimate the significance of factors that influenced the absorbance. The results are shown in the form of a Pareto chart (Fig. 3). Factors showing  $t > 2.12$  (indicated by the bars crossing the vertical line) had a significant effect on the response (at a 95% confidence level). The pyrolysis temperature (tA) and the combined pyrolysis and atomization temperatures (tAB) had significant effects on the response evaluated. The negative value for tA indicated that the response could be increased by decreasing the pyrolysis temperature. The positive effect for interaction between the pyrolysis and atomization temperatures (tAB) indicated that these factors were dependent on each other





**Fig. 2.** Atomic absorption spectra of eye shadow sample with LSBC based on background spectrum generation using: (a)  $\text{SiO}_2$ , (b)  $\text{SiO}_2:\text{TiO}_2$  (1:3, w/w), (c) mica, and (d) zeolite.



**Fig. 3.** Pareto chart generated from the experimental conditions and responses of the 23 factorial design. tA: Student's t-value for pyrolysis temperature; tB: Student's t-value for atomization temperature; tC: Student's t-value for sample weight; tAB, tBC, tAC, and tABC: Student's t-values for combined effects.

and could be optimized together. Considering these findings, a new experiment was designed in order to find the optimum values for the pyrolysis and atomization temperatures. New experiments using central composite design (CCD) were run using a fixed sample mass of around 0.15–0.25 mg. Fig. S4 shows a contour chart constructed using the levels of the factors investigated and the corresponding normalized integrated absorbances (corrected by LSBC using the zeolite reference spectrum). The brown circle

shows the region where the pyrolysis and atomization temperatures produced the best response, with the maximum indicated by the symbol “+”. Hence, the pyrolysis and atomization temperatures selected for the heating program of the graphite furnace atomizer for Sb determination in facial cosmetics were 1500 and 2100 °C, respectively. The optimized heating program is provided in Table 1.

### 3.3. Analytical method: features and application

Standard reference materials for facial cosmetics are not commercially available, while aqueous standards are readily accessible and enable simple calibration. The possibility of using calibration with aqueous standards for direct solid sample analysis of makeup samples was evaluated by comparing the slopes of analytical curves in the concentration range 0–4.8 ng Sb, constructed using standards in 0.1% (v/v)  $\text{HNO}_3$  (aqueous medium) or the soil CRM ( $\text{NO}_3$ )<sub>2</sub> + 2.5  $\mu\text{g}$   $\text{Mg}(\text{NO}_3)_2$  in 0.05% (m/v) Triton X-100. The slopes of the curves obtained were  $0.1440 \pm 0.0020$  and  $0.1503 \pm 0.0044$  s  $\text{ng}^{-1}$  using the aqueous and solid media, respectively, which were not significantly different at a 95% confidence level. The characteristic mass ( $m_0$ ) values calculated for the aqueous and solid media were  $30.9 \pm 0.19$  and  $29.9 \pm 3.8$  pg, respectively. These findings suggest that matrix effects were minimal, confirming the efficacy of the optimized heating program for use indirect solid sample analysis with calibration using aqueous standards. These results were close to  $m_0$  found in the literature (28 pg) for Sb at line 231.147 [16].

**Table 2**

Analytical figures of merit for Sb determination in facial cosmetic by HR-CS SS-GF AAS.

Parameter	Sb (217.581 nm)
LOD (mg kg <sup>-1</sup> )	0.3
LOQ (mg kg <sup>-1</sup> )	0.9
Linear working range (ng)	0.5–2.5
Characteristic mass (pg)	27.2 ± 0.6
r	0.9995

**Table 3**Results (mean ± SD) for Sb (mg kg<sup>-1</sup>) determined (n=3) in spiked eye shadow sample and Montana Soil II CRM (NIST 2711a) without and with LSBC using different precursors. Date between parentheses indicate recoveries in %.

Precursor	Sb ± SD (Recovery)	
	Eye shadow*	CRM NIST 2711a**
Without LSBC	13.2 ± 0.7 (151) t <sub>calculated</sub> = 11.0	38.6 ± 1.3 (162) t <sub>calculated</sub> = 19.7
SiO <sub>2</sub>	10.9 ± 0.6 (124) t <sub>calculated</sub> = 6.21	21.4 ± 1.3 (90) t <sub>calculated</sub> = 3.19
SiO <sub>2</sub> :TiO <sub>2</sub> 1:3 (m/m)	9.4 ± 0.4 (108) t <sub>calculated</sub> = 2.99	20.4 ± 0.3 (86) t <sub>calculated</sub> = 19.6
Mica	9.7 ± 0.6 (111) t <sub>calculated</sub> = 2.86	24.2 ± 1.8 (102) t <sub>calculated</sub> = 0.38
Zeolite	9.8 ± 0.5 (112) t <sub>calculated</sub> = 3.74	23.2 ± 0.8 (97) t <sub>calculated</sub> = 1.30

t<sub>critical</sub> (α=0.05; df=2)=4.30.\* Eye shadow sample spiked with 8.7 mg kg<sup>-1</sup> Sb.\*\* Certified value: 23.8 ± 1.4 mg kg<sup>-1</sup> Sb.**Table 4**

Recoveries (%) of Sb spiked in different samples. Values in parentheses indicate the RSD values.

Sample	Spike (mg kg <sup>-1</sup> )	Recovery (%)
Compact powder 1 - coral	6.2	82.5 ± 2.7 (3.3)
	8.7	90.1 ± 4.0 (4.5)
Blush 1 - pink	6.2	91.4 ± 4.5 (4.9)
	8.7	86.7 ± 5.1 (5.9)
Eye shadow 1 - purple	6.2	107.8 ± 4.8 (4.5)
	8.7	91.8 ± 3.8 (4.2)
Mica	6.2	94.1 ± 0.5 (0.5)
	8.7	97.6 ± 6.4 (6.6)
Zeolite	6.2	89.8 ± 2.4 (2.7)
	8.7	91.6 ± 6.5 (7.1)

The main figures of merit of the proposed method for Sb determination using the 217.581 nm absorption line were a dynamic working range of 0.50–2.25 ng Sb, correlation coefficient ≥ 0.9995, calibration sensitivity of 0.1518 s ng<sup>-1</sup>, detection limit of 0.3 mg kg<sup>-1</sup>, and quantification limit of 0.9 mg kg<sup>-1</sup>. The figures of merit are provided in Table 2. The effectiveness of background correction by LSBC using the zeolite reference spectrum was evaluated by analyzing a soil CRM and an eye shadow sample, both spiked with 8.7 mg kg<sup>-1</sup> Sb. For comparison, the CRM and the sample were also analyzed using LSBC with spectra for the SiO<sub>2</sub>, SiO<sub>2</sub>/TiO<sub>2</sub>, and mica precursors. The critical and calculated t-values obtained from unpaired t-test (Table 3) showed that more accurate results were obtained when mica and zeolite were employed as precursors for CRM, and SiO<sub>2</sub>/TiO<sub>2</sub>, mica, and zeolite were employed for spiked sample. Although accurate result was obtained when SiO<sub>2</sub> precursor was employed for CRM, there was an overcorrection of the spectrum, as shown in Fig. 2a. These findings reinforced the selection of mica or zeolite as the precursor for generating the SiO reference spectrum in the background correction by LSBC.

**Table 5**

Results (mean ± SD) for determination of Sb (n=3) in blush and eye shadow samples by the proposed method.

Sample	Sb (mg kg <sup>-1</sup> )
Blush 2 - orange	12.7 ± 0.2
Blush 3 - pink	14.5 ± 1.2
Eye shadow 2 - purple	9.1 ± 0.9

Accuracy studies were also carried out using recovery tests for compact powder, blush, eye shadow, mica, and zeolite samples spiked with 6.2 and 8.7 mg kg<sup>-1</sup> Sb. Recoveries of Sb added to the samples varied within the range 82–107% (Table 4). Relative standard deviations were ≤ 7.1%, which are acceptable when direct solid sample analysis is employed [22].

The method was then applied in analysis of thirteen commercial samples of eye shadow, blush, and compact powder. From thirteen analyzed samples, Sb was not detected in ten samples (blush, eye shadow and compact powder); three samples (two blush and one eye shadow) presented Sb concentration in the 9.1–14.5 mg kg<sup>-1</sup> range (Table 5). Only two samples presented Sb contents higher than the maximum acceptable level in cosmetics (10 mg kg<sup>-1</sup>) established by German and Canadian regulatory agencies [3,4].

#### 4. Conclusion

The LSBC algorithm is a valuable tool for background correction in the HR-CS SS-GF AAS technique, enabling appropriate precursors to be used for the generation of reference background spectra. An important finding was that the same chemical species could generate different background signals, as a function of time, because concomitant substances present in the samples acted as chemical modifiers and altered the formation time. Accurate determination of Sb in makeup samples could be achieved using precursors containing aluminum or titanium oxides that acted as chemical modifiers, retarding the SiO absorbance signals observed in the samples.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2016.09.017>.

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