Determination of Lead in Eye Shadow and Blush by High-Resolution Continuum Source Graphite Furnace Atomic Absorption Spectrometry Employing Direct Solid Sampling

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A espectrometria de absorção atômica em forno de grafite de alta resolução com fonte contínua (HR-CS GF AAS) é proposta para determinar Pb em sombra de olho e blush empregando a análise direta de sólidos. O emprego da mistura de modificadores químicos Pd(NO$_3$)$_2$ + Mg(NO$_3$)$_2$ possibilitou a calibração aquosa de 0,25 a 2,5 ng Pb ($r = 0,998$). O desempenho do método proposto foi avaliado por meio da análise de digeridos de sombra e de blush por espectrometria de absorção atômica em forno de grafite com fonte de linhas (LS GF AAS) como técnica comparativa. Os resultados obtidos por HR-CS GF AAS e LS GF AAS foram concordantes entre si a um nível de confiança de 95% (teste $t$ pareado). O limite de quantificação (massa seca) foi de 0,020 ng mg$^{-1}$. A concentração de Pb nas amostras de sombra de olho e de blush variou de 1,222 a 9,632 ng mg$^{-1}$ e de 0,362 a 28,091 ng mg$^{-1}$, respectivamente.

Direct solid sampling is proposed for Pb determination in eye shadow and blush samples by high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS). A mixture of Pd(NO$_3$)$_2$ + Mg(NO$_3$)$_2$ was employed as chemical modifier, and aqueous calibration (0.25-2.5 ng Pb, $r = 0.998$) was obtained. Accuracy of the determination of Pb in eye shadow and blush samples by the proposed method was verified by line source graphite furnace AAS as a comparative technique employing digested samples. The results obtained by the two methods were in agreement at a 95% confidence level (paired $t$-test). The limit of quantification (dry mass) was 0.020 ng mg$^{-1}$. The Pb content in the eye shadow and blush samples varied between 1.222 and 9.632 ng mg$^{-1}$ and 0.362 and 28.091 ng mg$^{-1}$, respectively.

Keywords: lead, cosmetics, direct solid sampling

Introduction

The global cosmetics industry is growing by 4.5% annually.$^1$ The worldwide market and the consumption of cosmetic products by adults and children require proficient quality control. In regard to facial cosmetics, they are applied to the skin and thus expose the user to the entire chemical and biological composition of the product.$^2$ The compositions of eye shadows and blushes are rather complex and may contain talc, pigments, mica, dyes, titanium dioxide, softeners, and binders among many other substances employed to ensure the fixing, brightness, and creaminess of the products.$^3$ Colored facial cosmetics may contain hazardous bio-accumulative metals, such as Pb, Ni, Cr, and As.$^4$ Metal dusts may ionize and result in percutaneous absorption of toxic metals.$^5$ Lead present in organic and some inorganic compounds can penetrate and pass through the skin into blood stream.$^6$ Considering the toxicity to humans of Pb and its compounds,$^7$ the US Food and Drug Administration (FDA) and the European Union’s Restriction on Hazardous Substances (RoHS) have established a maximum Pb level of 20 ng mg$^{-1}$ inorganic dyes employed in cosmetics.$^8$

The main spectrometric techniques for the determination of inorganic contaminants in facial cosmetics include flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GF AAS), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). Most published papers on this matter have been devoted to analyzing samples previously prepared by wet digestion with strong acids (HNO$_3$ and HF) and
oxidizing agents (e.g., H₂O₂) at high temperatures. Tetramethylammonium hydroxide (TMAH) was recently proposed for the partial solubilization of lipstick samples for Pb determination by GF AAS. Slurry-based sample preparation methods may be interesting but requires special attention to the use of an appropriate method of homogenization to assure representative sampling. These papers present the problems associated with analyzing hard-to-dissolve samples.

In this context, the development of analytical methods that follow the principles of green analytical chemistry to assess the presence of hazardous metals in facial cosmetics is attractive. Direct solid analysis based on a weight-and-assay method may be considered an environmentally friendly procedure because the energy, risk, and hazardous reagents in the sample preparation are eliminated and the waste generation and consumption of regular reagents are minimal.

The high-resolution continuous source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) technique is attractive due to its low detection limits, possibility of calibration with aqueous standards for direct solid analysis and improved background correction by the least-squares algorithm. However, the HR-CS GF AAS has been underexplored for the analysis of facial cosmetics: only two papers were found on the determination of Pb in lipstick samples.

This study reports on the development of a simple, fast and reliable method for the determination of Pb in eye shadow and blush samples by HR-CS GF AAS using direct solid sampling.

**Experimental**

**Instrumentation**

An Analytik Jena contrAA 700 high-resolution atomic absorption spectrometer equipped with a xenon short-arc lamp (XBO 301, 300 W, GLE, Berlin, Germany) as a continuum radiation source, a compact high-resolution monochromator comprising a prism and an Echelle grating with a spectral bandwidth lower than 2 pm per pixel in the far ultraviolet range and a charge-coupled device (CCD) array detector were used throughout the work. Pyrolytic graphite-coated solid sampling tubes without a dosing hole were used. High-purity (99.996%) argon (White Martins, São Paulo, Brazil) was used as both the purge and protective gas. Samples were weighed directly onto the graphite platform using a Sartorius WZ2PW micro-balance (Göttingen, Germany) with a precision of 0.001 mg. The optimized heating program of the graphite tube is shown in Table 1.

For the HR-CS GF AAS analyses, aqueous standards and modifier solutions were injected manually into the SSA 600 platform using micropipettes. A sample with a mass typically approximately 0.2-0.3 mg was introduced into the atomization compartment by using a pair of tweezers from the Analytik Jena SSA 600 automated solid sampling accessory. All of the measurements were made in triplicate and based on the peak volume integrated absorbance equivalent to three pixels. All of the atomic absorption measurements were carried out at the 283.306 nm line, and the absorbance values were normalized to 1.0 mg of sample.

For the evaluation of the accuracy of the proposed method, samples were digested in an Anton Paar Multiwave® microwave oven (Graz, Austria) equipped with 20 mL Teflon vessels and subsequently analyzed by line-source graphite furnace atomic absorption spectrometry (LS GF AAS). For this analysis, a PerkinElmer SIMAA™ 6000 simultaneous multi-element atomic absorption spectrometer equipped with a transversely heated graphite atomizer, longitudinal Zeeman-effect background correction and an AS-72 autosampler was employed. An electrode less discharge lamp was used at the analytical wavelength of 283.3 nm and an operating current of 450 mA.

All of the atomic absorption measurements by LS GF AAS were made in triplicate and based on the peak area mode. For the Pb measurements, the blank (20 µL), the Pd(NO₃)₂/Mg(NO₃)₂ modifier solution (5 µL), aqueous standards (20 µL) and sample digests (20 µL) were

<table>
<thead>
<tr>
<th>Step</th>
<th>Temperature / °C</th>
<th>Ramp / (°C s⁻¹)</th>
<th>Hold time / s</th>
<th>Argon flow rate / (L min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying 1</td>
<td>110</td>
<td>10</td>
<td>10</td>
<td>2.0</td>
</tr>
<tr>
<td>Drying 2</td>
<td>130</td>
<td>5</td>
<td>10</td>
<td>2.0</td>
</tr>
<tr>
<td>Pyrolysis</td>
<td>1400</td>
<td>50</td>
<td>30</td>
<td>2.0</td>
</tr>
<tr>
<td>Auto-zero*</td>
<td>1400</td>
<td>0</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>Atomization</td>
<td>2000</td>
<td>3000</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Cleaning</td>
<td>2500</td>
<td>500</td>
<td>5</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*Step to record a series of baseline spectra immediately before atomization.
sequentially dispensed into the graphite platform, and the following atomizer heating program (temperature, °C; ramp time, s; hold time, s) was run: drying - step 1 (110; 1; 30); drying - step 2 (130; 10; 30); pyrolysis - step 3 (1200; 10; 20); atomization - step 4 (2000; 0; 5); and cleaning - step 5 (2500; 1; 5). The argon flow rate was 250 mL min⁻¹ for steps 1, 2, 3 and 5, and the argon flow rate was set to zero during atomization.

Reagents, analytical solutions and samples

High-purity water (resistivity = 18.2 MΩ cm) obtained using a Millipore Rios 5® reverse osmosis and a Millipore Milli-Q Academic deionizer system (Millipore, Bedford, MA, USA) was used to prepare all of the solutions.

Modifier solutions containing 1000 mg L⁻¹ Pd(NO₃)₂ and 500 mg L⁻¹ Mg(NO₃)₂ were prepared by the appropriate dilutions of 10 g L⁻¹ Pd(NO₃)₂ and Mg(NO₃)₂ stock solutions (Merck, Darmstadt, Germany), respectively. These solutions were prepared in 0.05% (m/v) Triton X-100 (Malinckrodt Baker, Paris, KY, USA).

For the DSS HR-CS GF AAS calibration over the 0.25-2.5 ng Pb range, various aliquots of a 250 µg L⁻¹ aqueous standard were delivered onto the solid sampling tubes. This standard was prepared daily by the appropriate dilution of the 1000 mg L⁻¹ Pb stock solution (Titrisol®, Merck).

For the LS GF AAS calibration, aqueous standard solutions (5.0, 15.0, 25.0, 37.5 and 50.0 µg L⁻¹) were prepared daily in 0.14 mol L⁻¹ HNO₃ by the appropriate dilution of a 1000 mg L⁻¹ stock solution (Titrisol®, Merck). The autosampler wash solution was 0.14 mol L⁻¹ HNO₃ + 0.1% (v/v) Triton®X-100. All of the solutions were stored in high-density polypropylene bottles (Nalgene®, Rochester, USA).

Eye shadow and blush samples of various brands and in diverse colors were purchased in São Paulo State, Brazil. For the digestion of the samples, concentrated nitric acid (JT Baker, Mexico), hydrofluoric acid (Merck, Darmstadt, Germany) and hydrogen peroxide (Merck, Darmstadt, Germany) were used.

All of the plastic bottles and glassware materials were cleaned by soaking them in 10% (v/v) HNO₃ for at least 24 h and rinsing them abundantly in deionized water before use.

Procedure

The thermal behavior of Pb was evaluated in aqueous medium (1.5 ng Pb) and in eye shadow samples (0.2-0.3 mg) by means of pyrolysis and atomization temperature curves established in the absence and presence of 5.0 µg Pd(NO₃)₂, + 2.5 µg Mg(NO₃)₂ in 0.05% (m/v) Triton X-100. These modifier masses were obtained by delivering aliquots of 5 µL of each modifier solution. Samples and modifier solutions were sequentially injected into the platform. The surfactant Triton X-100 was used to reduce the surface tension between the solid and liquid phases and increase the interaction between the modifier and sample. The pyrolysis temperatures were varied within the range of 600 to 1600 °C, while the atomization temperature was fixed at 2000 °C. Afterwards, the optimized pyrolysis temperature was fixed, and the atomization was evaluated throughout a 1600 to 2400 °C range.

The linear working range was evaluated by means of the linear correlation coefficients (r) of curves employing aqueous standards with Pb contents in the range of 0.25-2.5 ng. The sensitivity was checked by calculating the characteristic mass, and the limits of detection (LOD) and quantification (LOQ) were determined according to the IUPAC recommendation.²⁰

Studies on the homogeneity and the dependence of the minimum mass on the precision were evaluated by determining the Pb in eye shadow samples within the 0.05-1.0 mg mass range. This large interval was divided into ten subintervals as follows: 0.05-0.10 mg; 0.10-0.20 mg; 0.20-0.30 mg; 0.30-0.40 mg; 0.40-0.50 mg; 0.50-0.60 mg; 0.60-0.70 mg; 0.70-0.80 mg; 0.80-0.90 mg; and 0.90-1.0 mg. Each interval was evaluated in quintuplicate (n = 5).

Samples were mineralized in triplicate in a closed-vessel microwave-assisted acid-digestion system. A mass of 0.20 g of sample was accurately weighed and transferred to a microwave Teflon vessel followed by 3 mL of concentrated nitric acid, 2 mL of hydrofluoric acid and 1 mL of 30% (m/m) hydrogen peroxide. The mixture was then heated using the following optimized power/time program: step 1, 0-900 W, 15 min ramp; step 2, 900 W, 30 min hold; step 3, 900-0 W, 20 min ramp; and step 4 (ventilation), 0 W, 5 min hold. The temperature of 200 °C was reached by using 900 W. After the digestion, the digests were transferred to 50 mL Teflon tubes and heated in a block digestor at 150 °C for 4 h to eliminate the remaining hydrofluoric acid. This procedure was adopted because the addition of boric acid induced precipitation that could occlude the analyte. The high K content in the samples (from potassium sorbate) may contribute to the formation of KBF₄, which has a relatively low solubility. It should be commented that a heating time less than 4 h was not enough for the complete removal of the hydrofluoric acid. This was checked by exposing a small piece of glass to the solution and observing the eventual reaction of the hydrofluoric acid on the glass surface. If lower temperatures were used, extra heating time was required. It should be stressed that...
150 °C was selected by considering the waiting time for the removal of the hydrofluoric acid and a low probability of losing Pb due to the high melting and boiling temperatures for both its chlorides and nitrates. After cooling, the resulting digests were transferred to 25 mL volumetric flasks, and the volume completed with water.

**Results and Discussion**

Considering the relatively high concentrations of Pb that were expected in the eye shadow samples, and the possibility of selecting analytical lines with varying sensitivities in HR-CS AAS, the secondary line at 283.306 nm was selected for all of the experiments. Calibration with aqueous standards was evaluated because solid standards and certified reference materials for blushes and eye shadows are not commercially available. Hence, the heating program of the atomizer was optimized by studying the thermal behavior of Pb in aqueous and solid medium to check for matrix effects.

The thermal behavior of Pb was investigated by means of pyrolysis and atomization temperature curves built up in 1% (v/v) nitric acid and sample media without a modifier and in the presence of Pd(NO_3)_2/Mg(NO_3)_2 as a modifier. Pyrolysis and atomization temperature curves (Figure 1) were employed to determine the optimum pyrolysis and atomization temperatures for Pb in each media.

The presence of chemical modifier on analyte stabilization was relevant. The analyte can be stabilized in the sample up to ca. 1000 °C (Figure 1c) and 1400 °C (Figure 1d) in the absence and presence of Pd(NO_3)_2/Mg(NO_3)_2, respectively. However, preliminary experiments showed a slight formation of residue after each analytical cycle (firing), which deteriorated subsequent measurements. These cumbersome were circumvented by using Pb/Mg as modifier since higher pyrolysis temperature helps to maximize the elimination of components commonly present in most eye shadows and blushes (petroleum jelly, fats, waxes, lanolin, dyes, preservatives, silica, TiO_2, zinc stearate, and pigments).

For atomization temperature ≥ 1800 °C, the recorded wavelength and time-resolved absorbance spectra in the vicinity of the Pb absorption line showed fine structures due to SiO molecules (Figure 2). The background is not visible at atomization temperatures around 1600 °C, but the transient signals did not return to the baseline, suggesting higher atomization temperature was necessary. In spite of the discontinuous events at atomization temperatures higher 1600 °C, interferences were efficiently removed using the least-squares background correction (LSBC) method: the software of the spectrometer stores a reference spectrum and subtracts it from the recorded spectra of the samples by means of a least-squares algorithm. Here the spectrum of a SiO molecule was recorded (Figure 2a) and subsequently...
Determination of Lead in Eye Shadow and Blush


144

subtracted from each sample (Figure 2b) using a least-squares algorithm.

The background-corrected spectrum is shown in Figure 2c. When eye shadow sample was analyzed without correction, the determined Pb concentrations were typically 17% higher than those obtained with LSBC. These findings reinforce the need for LSBC for accurate determination of Pb in all workable samples.

Inspection of the atomization curves in the presence of a modifier indicated that the maximum sensitivity was attained at 1800 ºC (Figure 1b e 1d). However, this temperature resulted in broadened transient signals and poor precision. A better profile for the atomic absorption transient peak (fast peak appearance and baseline restoration) and lower relative standard deviation (RSD) were observed for measurements at 2000 ºC, without a significant loss in the sensitivity. Considering these aspects, the selected pyrolysis and atomization temperatures were 1400 ºC and 2000 ºC, respectively.

The optimized heating program of the atomizer for Pb determination in eye shadow and blush samples is depicted in Table 1. The running time of this program is 132 s, but the entire time for each absorbance measurement is approximately 4 min due to the time spent weighing and transferring the sample. Considering that the 4 min analytical cycle includes the in situ preparation of difficult samples, this time consumption is much more favorable than methods involving conventional sample preparation techniques based on wet-ashing.

Considering there is no blush and eye shadow certified reference materials, authors used aqueous standard solution and an eye shadow sample (Adult 3, Table 2) to calculate the characteristic masses. This sample was previously prepared by a well-established and worldwide accepted method for digestion: a microwave-assisted digestion in closed vessels. The Pb content (5.183 ng mg⁻¹) in the digested sample was determined by LS GF AAS and ICP-MS and was taken as ‘target value’. It should be mentioned that the characteristic masses calculated for aqueous and solid media were 10.8 pg and 10.7 pg of Pb, respectively. The closer the characteristic masses are, the better the effectiveness of the aqueous standard calibration for the analysis of solid samples, which suggests that the optimized heating program of the atomizer was adequate to minimize any matrix effects. Using the optimized heating program in Table 1, aqueous calibrations over a 0.25-2.5 ng Pb mass interval were consistently obtained, and the linear correlation coefficients were approximately 0.9965. The LOD and LOQ (dry mass) were 0.006 and 0.020 ng mg⁻¹, respectively.

In DSS HR-CS GF AAS, the accuracy and precision may be influenced by the sample size and homogeneity; a large amount of sample may impair the release of the analyte from the matrix and/or make the analyte vaporization difficult. However, if the analyte is not homogeneously distributed within the matrix, a small sample size may not be representative of the sample. Studies on homogeneity and minimum mass were then conducted by analyzing different masses (0.05-1.0 mg) of an eye shadow sample. A plot of the Pb concentration versus the mass of the sample, Adult1 eye shadow that contains 4.981 ± 0.722 ng mg⁻¹ is shown in Figure 3.

It should be mentioned that the Pb concentration in this sample was previously determined by LS GF AAS. Solid and dashed lines correspond to the average and standard deviation (± 1σ), respectively. Sample masses within the 0.05-0.4 mg range furnished reasonable results. However, the most accurate and precise results were observed for sample masses in the 0.2-0.3 mg range. In general, the greater the sample mass, the lower the RSD of the measurements. Masses < 0.05 mg were not studied due to the difficulties in handling very small amounts of samples manually. Concentrations below the expected value (4.981 ng mg⁻¹) were found for masses > 0.4 mg. Samples with higher sample masses may alter the efficiency of the atomization process by occluding the analyte inside the

Figure 2. Least-squares background correction technique for Pb at 283.306 nm (a) reference spectrum of SiO, (b) spectrum of the eye shadow sample (1.0 ng mg⁻¹ Pb) - interference of SiO molecular absorption bands and (c) net absorbance spectrum for Pb after correction with LSBC. The dotted line indicates the position of the Pb absorption line.
matrix. Direct analysis of approximately 0.20-0.30 mg was subsequently selected after considering the different Pb concentrations in the samples, the working range of the calibration curve and the measurements that provided high precision and accuracy. It should be emphasized that the sample Adult1 eye shadow presented as homogeneous. The homogeneity was assessed by calculating the homogeneity factor $H_e = S_H \times m^{1/2}$. In this equation, $S_H$ corresponds to the sampling error that can be directly correlated to the RSD of analyses of a sample mass $m$ (in mg). A sample with a $H_e < 10$ is considered homogeneous. The micro-homogeneity was evaluated by plotting $H_e$ against the mass interval. The sample Adult 1 eye shadow was considered to be homogeneous for all of the sample mass intervals because the $H_e$ factors calculated were < 10 (in the Supplementary Information (SI) section, Figure S1).

These findings were also observed for most samples presenting similar Pb concentrations to that of the sample Adult1 eye shadow. Additionally, the higher the Pb content in the sample, the greater the probability of producing a homogeneous distribution of the analyte in the material. The proposed procedure was then applied for the determination of the Pb in eye shadows and blushes of different brands and of diverse colors available in most commercial market places. Because no sample preparation was needed, samples were transferred directly from the packaging to the graphite atomizer. Measurements were made at 283.306 nm using a peak volume selected absorbance equivalent to 3 pixels, and calibration with aqueous standards was adopted.

After optimization, all of the samples were analyzed, and the Pb concentrations that were determined varied in the ranges of 1.222-9.632 ng mg$^{-1}$ (eye shadows) and 0.362-28.091 ng mg$^{-1}$ (blushes). These concentrations are comparable to the values usually found in the literature$^{24}$ for eye shadows (0.85-6.90 ng mg$^{-1}$). The RSD ($n = 3$) was 8.2% for a sample containing 0.997 ng mg$^{-1}$ Pb, and the LOQ (dry mass) was 0.020 ng g$^{-1}$. For comparison purposes, samples were also analyzed by line-source GF AAS, which employed digested samples. The results were in agreement at a 95% confidence level (paired $t$-test) with those obtained by DSS HR-CS GF AAS (Table 2).

Table 2. Results (ng mg$^{-1}$) expressed as the average ± standard deviation for the Pb in eye shadow and blush samples determined ($n = 3$) by the proposed procedure (DSS HR-CS GF AAS) and by a comparative technique (LS GF AAS)

<table>
<thead>
<tr>
<th>Sample</th>
<th>DSS HR-CS GF AAS</th>
<th>LS GF AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eye shadow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adult1</td>
<td>4.748 ± 0.331</td>
<td>4.981 ± 0.722</td>
</tr>
<tr>
<td>Adult2</td>
<td>9.632 ± 0.491</td>
<td>8.635 ± 0.663</td>
</tr>
<tr>
<td>Adult3</td>
<td>5.022 ± 0.378</td>
<td>5.183 ± 0.229</td>
</tr>
<tr>
<td>Infant1</td>
<td>5.036 ± 0.346</td>
<td>5.541 ± 0.308</td>
</tr>
<tr>
<td>Blush</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adult1</td>
<td>6.901 ± 0.466</td>
<td>6.313 ± 0.137</td>
</tr>
<tr>
<td>Adult2</td>
<td>6.646 ± 0.821</td>
<td>6.711 ± 0.742</td>
</tr>
<tr>
<td>Infant1</td>
<td>7.001 ± 0.402</td>
<td>7.688 ± 0.456</td>
</tr>
<tr>
<td>Infant2</td>
<td>7.080 ± 0.294</td>
<td>7.503 ± 0.236</td>
</tr>
</tbody>
</table>

Sixty adult samples and twenty-four samples for children (Supplementary Information) of different brands and colors were also analyzed. The levels of Pb found in makeup for children (4.187-7.344 ng mg$^{-1}$) and adult (0.997-9.632 ng mg$^{-1}$) eye shadows were close (Table S1). It should be mentioned that the Pb levels in all of the blushes for children (4.779-28.091 ng mg$^{-1}$) were higher than in the blushes for adults (0.362-8.369 ng mg$^{-1}$) (Table S2). Considering that Pb toxicity depends on a number of factors such as age, sex and weight, children are more vulnerable to the effects of Pb than adults due to their frequency of use and long-term exposure. The US FDA established a maximum acceptable level of Pb (20 ng mg$^{-1}$) in synthetic and artificial dyes employed as color additives. Considering that the total amount of a certain contaminant is dependent on the impurities present in each component of the makeup and the high toxicity of Pb and its effects on human health, regulatory agencies should also establish a maximum acceptable value for toxic metals in end user products.

**Conclusions**

This work presents a simple, reliable and robust method for the Pb determination in eye shadows and blushes through HR-CS GF AAS employing direct solid sampling. The proposed method involves short-run analysis...
of samples transferred directly from their packages to the atomizer container. Calibration with aqueous standards was feasible, representing an attractive feature of this technique. The RSD was 8.2%, and the LOQ was 0.020 ng g\(^{-1}\) Pb. The direct solid sampling approach may be considered a sustainable clean method because sample preparation with hazardous reagents is not required, the consumption of reagents is notably low, the generation of waste is irrelevant, and the time consumption is shorter than that of other methods.

**Supplementary Information**

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

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**References**

2. Lundov, M. D.; Moesby, L.; Zachariae, C.; Johansen, J. D.; Contact Dermatitis 2009, 60, 70.

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