



# Determination of Pb and Cr in sunscreen samples by high-resolution continuum source graphite furnace atomic absorption spectrometry and direct analysis



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## ABSTRACT

A method has been developed for the determination of Cr and Pb in sunscreen samples by high-resolution continuum source graphite furnace atomic absorption spectrometry and direct analysis (HR-CS DS-GF AAS). Eleven commercial samples of different brands and different factors of sun protection sunscreen were analysed. For optimisation of the furnace temperature programme, pyrolysis and atomisation curves with M1 sunscreen sample were performed using a chemical modifier (0.05% Pd + 0.03% Mg + 0.05% Triton X-100) for Pb and without a modifier for Cr. The figures of merit obtained were: characteristic mass of 10 pg and 2.5 pg and limit of detection (LOD) of 3.0  $\mu\text{g kg}^{-1}$  and 1.0  $\mu\text{g kg}^{-1}$  for Pb and Cr, respectively, based on a sample mass of 4.5 mg. Relative standard deviation (RSD) values were lower than 9%, which are acceptable for direct analysis. For assessment of the accuracy of the method, sunscreen samples were digested. The results obtained with direct determination of Pb and Cr in sunscreen samples and with acid digestion were statistically accordant, using the calibration with aqueous standards, showing that this calibration method is suitable for this application. The method developed for the analysis of sunscreen samples is accurate, simple, fast and suitable for routine application.

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## 1. Introduction

Sunscreen products are intended to prevent the skin from the harmful effects of excessive exposure to ultraviolet sunlight, like protecting the skin from sunburn, reducing premature skin ageing and reducing skin cancer risk [1,2]. There are two classes of sunscreen products based on the scattering process: organic and inorganic. Organic sunscreens contain chemical filters that absorb high intensity ultraviolet rays, while inorganic sunscreens act by reflecting these ultraviolet rays [3–5].

Sunscreens are included in the cosmetics category, since these are preparations consisting of natural or synthetic substances for external use on various parts of the human body. Cosmetics can be a source of exposure to harmful elements through the absorption of these elements into the skin. A number of compounds may accumulate in human body, which can cause severe damage, even at low concentrations [6,7]. Pb, for example, may cause gastrointestinal, reproductive, neurological and renal problems and increases the risk of cancer [8]. Cr, in its oxidation state (III), is essential to our diet, since it does not exceed appropriate limits. In the oxidation state (VI), Cr is a potential carcinogen [9].

In Brazil, the regulatory authority is the National Health Surveillance Agency (ANVISA), which has established lists of heavy metals in organic dyes used for cosmetics [10]. According to ANVISA, the presence of Cr is not allowed, while 20  $\mu\text{g g}^{-1}$  of Pb is permitted only in organic dyes. Many countries have their own legislation to regulate the level of heavy metals. The Association of Southeast Asian Nations (ASEAN) proposed a directive that limits and forbids the presence of several compounds in cosmetics, including ultraviolet absorbers and dyes [7,11]. The Federal Agency of the United States, the Food and Drug Administration (FDA), allows a limit for Pb in the range of 10 to 20  $\mu\text{g g}^{-1}$  for dyes in cosmetics [7,12]. Canada, through the Federal Department of Health Canada, stipulated a maximum of 10  $\mu\text{g g}^{-1}$  of Pb in cosmetics [7,13]. The Bureau of Indian Standards (BSI) and the German Government permitted a maximum of 20  $\mu\text{g g}^{-1}$  of Pb in synthetic and organic colours [7,14]. The presence of Cr in cosmetic products is not allowed in these countries. Thus, the monitoring of these elements by highly sensitive, fast and reliable analytical methods is extremely necessary for an effective control. As can be seen in the study by Ng et al. [7], the development of a certified reference material for products such as sunscreens is important to give support to applicable government regulations, allowing the correct control of harmful elements.

Many compounds used in the manufacture of sunscreen may not be pure, which can impact on the quality and human exposure to heavy metals [2,15]. In this case, monitoring of the final product is essential

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to maintain the concentration of impurities below the limit established by legislation. To date, no formal method for the determination of inorganic contaminants in sunscreen has been established [2]. Zachariadis and Sahaniadou reported that metals such as Cr and Pb can be potentially allergenic [2].

In the literature, various analytical techniques have been used for the determination of trace elements in sunscreens and skin creams: flame atomic absorption spectrometry (FAAS) [15–17], electrothermal atomic absorption spectrometry (ETAAS) [18], inductively coupled plasma optical emission spectrometry (ICP-OES) [2,11], inductively coupled plasma-mass spectrometry (ICP-MS) [7,19–21], laser-induced breakdown spectroscopy (LIBS) [22] and high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS) [23].

The initial procedures of an analytical method are responsible for the accuracy of the chemical information. The sample preparation phases required for the determination of metals in complex matrices through spectroanalytical techniques include digestion (wet and microwave-assisted) and slurry [24]. Zachariadis et al. [2] determined Al, Zn, Mg, Fe, Mn, Cu, Cr and Pb in five samples of sunscreens using by ICP OES. The authors tested two pre-treatment procedures: Acid digestion in closed pressurised vessels and the direct introduction of samples in the form of emulsified slurry. Bocca et al. [15] determined Cd, Co, Cr, Cu, Hg, Ir, Mn, Ni, Pb, Pd, Pt, Rh and V in body cream samples using ICP-MS with microwave-assisted acid digestion. Chukwujindu et al. [12] determined Cd, Pb, Ni, Cr, Cu, Co, Fe, Mn, Zn and Al by F-AAS in skin-lightening creams using wet-acid digestion in Teflon vessels.

Many advantages of the HR-CS AAS technique can be found in the literature [25]. One of them is the ability to use direct sampling analysis, which reduces the sample preparation time, improves the limits of detection and decreases the risk of sample contamination when samples are not diluted, as well as avoiding the use of acids and other aggressive reagents [26]. Another advantage of HR-CS AAS is the capability to detect spectral interferences due to the visibility of entire spectral environment and three-dimensional image, which is not possible in GF AAS [25–28]. Calibration with aqueous standards is also a possibility in a most cases. The presence of a high-resolution double monochromator and a linear charge-couple device in HR-CS AAS technique allows to obtain better LOD when compared with traditional GF AAS technique [25,29]. Therefore, this appears to be a good alternative for the determination of trace elements in sunscreen samples. To the best of our knowledge, the determination of Cr and Pb in sunscreen samples using direct analysis by HR-CS DS-GF AAS has not been published until now.

The goal of this work was the development of a simple, fast, and accurate analytical method using HR-CS DS-GF AAS, which can be applied routinely in the determination of Cr and Pb in sunscreen samples. The samples were weighed directly onto the solid sampling platforms and introduced into the graphite tube for analysis. The accuracy of the method has been investigated using wet-acid digestion.

## 2. Experimental

### 2.1. Instrumentation

All measurements were carried out using in a Model contra 700 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Germany), equipped with a transversely-heated graphite tube atomiser. The contra 700 was equipped with a xenon short-arc lamp with a nominal power of 300 W operating in a hot-spot mode. The high-resolution double monochromator had a prism pre-monochromator, a high-resolution echelle monochromator and a linear charge coupled device (CCD) array detector with 588 pixels, 200 of which were used for analytical purposes. The analytical lines at 283.306 nm for Pb and 359.349 nm for Cr were used. Atomic absorption was measured using the centre pixel (CP) and the two adjacent pixels (CP  $\pm$  1), corresponding to a spectral interval of 4.8 pm for Pb and

5.7 pm for Cr. The experiments were carried out using pyrolytically-coated solid sampling graphite tubes without a dosing hole (Analytik Jena Part no. 407-A81.303) and solid sampling graphite platforms (Analytik Jena Part no. 407-152.023). A M2P microbalance (Sartorius, Göttingen, Germany) was used for weighing the sunscreen samples directly onto the solid sampling (SS) platforms, which were introduced into the graphite tube using a pair of pre-adjusted pair of tweezers that is part of the SSA 6 manual solid sampling accessory (Analytik Jena AG). The sample mass was transmitted to the instrument's computer to calculate the integrated absorbance normalised to a sample mass of 1.0 mg after each measurement. The aqueous standards were injected manually onto the platform using a micropipette. Argon with a purity of 99.996% (White Martins, São Paulo, Brazil) has used as a purge gas with a flow rate of 2.0 L min<sup>-1</sup> during all stages, except during atomisation, when the flow was stopped for the determination of Pb and Cr, respectively. The optimum parameters for the graphite furnace temperature for both elements are shown in Table 1.

### 2.2. Reagents and solutions

Analytical grade reagents were used exclusively. Deionised water with a specific resistivity of 18 M $\Omega$  cm<sup>-1</sup> from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used for the preparation of standards.

The nitric acid (Merck, Darmstadt, Germany) used to prepare the standard solutions was further purified by sub-boiling distillation in a quartz sub-boiling still (Kürner Analysentechnik, Rosenheim, Germany). All containers and glassware were soaked in 1.4 mol L<sup>-1</sup> nitric acid for 24 h and rinsed with deionised water before use.

The Pb and Cr stock standard solutions (1000 mg L<sup>-1</sup>) were prepared from Specsol, Brazil). The working standards were prepared by serial dilution of the stock solutions with the addition of 0.014 mol L<sup>-1</sup> nitric acid (Merck, Germany). The chemical modifier tested was a solution of 0.05% (m/v) Pd(NO<sub>3</sub>)<sub>2</sub> + 0.03% Mg(NO<sub>3</sub>)<sub>2</sub> in both 0.05% (v/v) Triton X-100 from (Merck, Germany, and Triton X-100 from Union Carbide). The use of Triton X-100 was necessary to increase the interaction between samples and the modifier [30]. The following reagents were used for sample digestion: 37% (v/v) HCl, 65% (v/v) HNO<sub>3</sub> and 40% (v/v) HF all from (Merck, Germany).

### 2.3. Samples and direct analysis of sunscreen samples

Eleven sunscreen samples were purchased from local supermarkets in Porto Alegre, Brazil, during 2015. The samples M1 and M9 (FPS15), M4, M6 and M10 (FPS-30), M2 (FPS-45), M3 and M11 (FPS-50), M5, M7 and M8 (FPS-100). The samples M6, M7 and M8 contained colour additives.

The sample mass (0.3 to 4.5 mg) was weighed directly on the platform and introduced into the graphite tube of HR-CS DS-GF AAS for the determination of Pb and Cr.

**Table 1**

Graphite furnace temperature programme for the determination of Pb and Cr in sunscreen samples by HR-CS DS-GF AAS.

Stage	Temperature (°C)	Ramp (°C s <sup>-1</sup> )	Hold time (s)	Gas flow rate (L min <sup>-1</sup> )
Drying 1	90	10	20	2
Drying 2	130	10	40	2
Pyrolysis	1200 <sup>a</sup> /1300 <sup>b</sup>	300	30	2
Atomization	2100 <sup>a</sup> /2600 <sup>b</sup>	3000	10	0
Cleaning	2650	500	6	2

<sup>a</sup> Pb.

<sup>b</sup> Cr.

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