

COSMETIC PRODUCTS FOR CHILDREN AND ADULTS – DETERMINATION OF As, Ni, Pb AND Zn CONTENTS

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ABSTRACT

The objective of this work was to determine the concentration of potentially toxic elements in different cosmetic products, using simple and accessible digestion methodologies, and spectroscopic techniques. A total of twelve products were selected, purchased and analyzed, which include blush (BL), eye shadow (SH), face powder (PO) and powdered paint for children (PP). The samples were dried (at 100°C), crushed and homogenized. Two methodologies were used for digestion. The contents of Ni, Pb and Zn were quantified by atomic absorption spectrometry flame (FAAS), and the contents of As by atomic absorption spectrometry with electrothermal atomization in a graphite oven (GFAAS). In general, the samples showed contents below the detection limit (LOD) for Ni, Pb, As and Zn. However, some PP samples showed Zn contents between 2 ± 1 and 442 ± 32 mg L⁻¹. This result is probably due to the use of some natural or inorganic pigments, and suggests the following actions: (1) regular monitoring of potentially toxic elements in PP products; (2) new studies on Zn levels in cosmetic products for children; and (3) the creation of legislation to regulate the composition of PP products.

Keywords: Blush. Eye shadow. Face powder. Powdered paint. Atomic absorption spectrometry flame. Atomic absorption spectrometer with electrothermal atomization in a graphite oven.

1 Introduction

Cosmetics are substances used as personal care products to enhance or protect the appearance or mask the odor of the human body [1]. According to European Regulation (EC) No.

1223/2009 [2], the cosmetics are “any substance or mixture intended to be placed in contact with the external parts of the human body (epidermis, hair system, nails, lips, and external genital organs) or with the teeth and the mucous membranes of

the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance, protecting them, keeping them in good condition or correcting body odors” [2].

During the last few decades, the use of cosmetic products has increased around the world [3]. Its products have been commonly used by millions of consumers of all types, regardless of age, socio-economic or cultural lifestyles around the world [4]. The increase in the consumption of these products has also been observed among children (0 to 10 years old).

As a result, there was an increase in the diversity of products and brands, and the lack of control over the composition, origin of ingredients applied in the composition, quality, among others is a growing concern. Cosmetic products used for children are as numerous as they are diverse. There are in the literature studies about children's consumption and exposure to cosmetic products [4-6]. However, very little information about the risks of these products is available, especially in relation to the inorganic composition. According to Bocca et al. [7], the composition of cosmetic products is rather complex and may contain hazardous bio-accumulative metals.

The most used analytical approach to the quantification of metal content in cosmetics, in the absence of official methods, is the digestion with acids (HNO_3) and H_2O_2 [8-11] followed by

instrumental determination using inductively coupled plasma optical emission spectrometry (ICP OES) [12], atomic absorption spectrophotometer flame (FAAS) [9-11;13], inductively coupled plasma-mass spectrometry (ICP-MS) [14], or other techniques.

This study reports on the development of a simple and fast methodology for the digestion of cosmetic products. The aim of this study was to determine the concentration of potentially toxic elements as Nickel (Ni), Lead (Pb), Zinc (Zn), and Arsenic (As) in different cosmetics such as blush (BL), eyes shadow (SH), face powder (PO) and powdered paint for children (PP), using simple digestion methodologies like atomic absorption spectrometry flame (FAAS), and atomic absorption spectrometry in a graphite oven (GFAAS) techniques. The Pb and As were selected in this study because they are considered toxic even at low concentrations, and they can be bioaccumulated in the organism [7]. The Ni is involved in allergic dermatitis [15]. The Zn has been frequently used in cosmetic products, such as Zn oxide and Zn stearate [3].

2 Methodology

2.1 Cosmetic Product Samples

A total of twelve cosmetic product samples (Table 1) were selected and purchased in local markets in Pato Branco, Paraná, Brazil. The samples analyzed in this work include BL, SH, PO, and PP. The BL, SH and PO selected samples were imported from China and the PP from Brazil.

The BL, SH, and PO samples were analyzed in two shades, light and dark. The nomenclature adopted was: BLl (light blush), BLd (dark blush), SHl (light eye shadow), SHd (dark eye shadow), POl (light face powder), and POd (dark face powder).

The PP samples were identified according to the colors: PPl (purple powdered paint), PPy (yellow powdered paint), PPb (blue powdered paint), PPo (orange powdered paint), PPpi (pink powdered paint), and PPg (green powdered paint). In table 1 are presented the identification of the samples analyzed in this work.

Table 1. Identification of cosmetic products

Identification Sample	Cosmetic Product	Shade or Color
BLl	Blush	Light
BLd	Blush	Dark
SHl	Eye shadow	Light
SHd	Eye shadow	Dark
POl	Face powder	Light
POd	Face powder	Dark
PPl	Powdered paint	Purple
PPy	Powdered paint	Yellow
PPb	Powdered paint	Blue
PPo	Powdered paint	Orange
PPpi	Powdered paint	Pink
PPg	Powdered paint	Green

2.2 Reagents and Solutions

Standard solutions for calibration curves were prepared by serial dilution of commercial stock solutions (1000 mg L⁻¹) of Grupo Química. The reagents HNO₃ and H₂O₂ were of analytical grade unless otherwise specified. Ultra-pure water (18MΩ) was obtained from a Milli-Q purification system (Merk Millipore, Darmstadt, Germany). A Digital Ultrasonic Cleaner CD-4860 ultrasonic bath (Gnatus, São Paulo, Brazil) was used to sample sonication in methodology 2. All laboratory glassware was previously decontaminated with 10% (v v⁻¹) of HNO₃.

solution for 24 hours. Before use, these materials were rinsed abundantly with deionized water.

2.3 Sample Preparation

Initially, the cosmetic samples were dried (at 100°C), until you get constant weight, grounded and homogenized. For sample digestion, two methodologies were applied. The methodology 1 used in this study was based on procedures recommended by Ullah et al [16] with some modifications, and the methodology 2 is a suggestion of this work.

Methodology 1 – After drying (at 100°C) the cosmetic sample was calcined at 600°C for 2 hours [11]. After cooling to room temperature (at desiccator), the residual ashes (≈ 0.100 g) were digested with 2mL of HNO_3 1 mol L^{-1} at 130°C in a digester block to about 1mL. Finally, the solution was quantitatively transferred to Falcon tubes and the volumes completed with ultra-pure water (MiliQ) up to 25mL [14]. All experiment was carried out in triplicate ($n = 3$). Blank was treated in the same procedure. The solution obtained after digestion was used for analytical determinations, which were carried out in triplicate.

Methodology 2 – A pre-digestion with 1mL of 35% (v v⁻¹) H_2O_2 and 0.100g of cosmetic sample (1 hour of repose) was performed after drying (100°C). Subsequently, it was added 1mL

HNO_3 and the solution was put into the ultrasonic bath for 30 minutes at 60°C. After the vessel was to a digester block at 120°C to about 1mL. Finally, the solution was quantitatively transferred to Falcon tubes and the volumes completed with ultra-pure water (MiliQ) up to 25mL. All experiment was carried out in triplicate ($n = 3$). Blank was treated in the same procedure. The solution obtained after digestion was used for analytical determinations, which were carried out in triplicate.

2.4 Instrumental Parameters

Ni, Pb, and Zn were quantified by FAAS and As was quantified by GFAAS using a Perkin Elmer PinAAcle 900T spectrometer (Norwalk, CT, USA) operated at 232.00 nm (Ni), 283.31 nm (Pb), 213.86 nm (Zn), and 193.70 nm (As).

The oven temperature program applied in GFAAS is given in Table 2. A monoelementary hollow cathode lamp from Perkin Elmer was used. The flame composition was air-acetylene. Calibration curves of the Ni, Zn, Pb, and As analytes were prepared using standard solutions.

Table 2. GFAAS program for As analysis

Step	Temperature (°C)	Time ramp (s)	Time hold (s)
Drying	110	1	30
Drying	130	15	30
Pyrolysis	1200	10	20
Atomization	2000	0	5
Cleaning	2450	1	3

2.5 Detection and Quantification Limits

The limits of detection (LOD) and quantification (LOQ) were calculated following the IUPAC approach [15], which consists in analyzing the blank sample, calculating the standard deviation and expressing the result as the mean plus 3- and 10-times standard deviation for LOD and LOQ, respectively:

$$LOD = \frac{3 \times SD^{blank}}{b} \quad (1)$$

$$LOQ = \frac{10 \times SD^{blank}}{b} \quad (2)$$

where SD is the standard deviation for ten blank measurements (using an empty platform) and b is the angular coefficient of the calibration curve.

2.6 Moisture and Ashes Content Determination

After drying at 100°C, the cosmetic sample was calcined in a muffle oven at 600°C for 2 hours. Subsequently, the calcined sample was cooled in a desiccator. Finally, the mass of the sample was measured, and the moisture content (MC) and the ashes content (AC) were calculated using the formulas:

$$MC = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100 \quad (3)$$

$$AC = \frac{M_{dry}}{M_{wet}} \times 100 \quad (4)$$

where MC is the moisture content of the sample, M_{wet} is the wet weight and M_{dry} is the dry weight.

3 Results and Discussion

3.1 Instrumental Parameters

The inorganic elements may exist as impurities in the raw ingredients or as products of the manufacturing process of cosmetics [18]. Among the harmful elements that elicit concern are include Ni,[19] Pb, As,[20] and Zn [18-21].

The Ni, Pb, and As are naturally present in iron oxide pigments and other raw materials used in the cosmetic products

during the manufacturing [7, 22]. Although, currently there is no regulation on the tolerances of the toxic elements in iron oxide pigment, the quantification of the Pb, As, and Ni contents in cosmetic products are of great importance for the control of its quality and for the safety of its applications [22].

Table 3. Results obtained (mg L⁻¹) in the determination of Ni, Pb, Zn and As in cosmetic products by two methodologies and employing the FAAS and GFAAS.

Samples	Ni		Pb		Zn		As	
	-----mg L ⁻¹ -----							
	M1	M2	M1	M2	M1	M2	M1	M2
BLI	< 0.038	< 0.025	< 0.023	< 0.027	< 0.334	< 0.088	< 0.049	< 0.008
BLd	< 0.038	< 0.025	< 0.023	< 0.027	< 0.334	< 0.088	< 0.049	< 0.008
SHI	< 0.038	< 0.025	< 0.023	< 0.027	< 0.334	< 0.088	< 0.049	< 0.008
SHd	< 0.038	< 0.025	< 0.023	< 0.027	< 0.334	< 0.088	< 0.049	< 0.008
POI	< 0.038	< 0.025	< 0.023	< 0.027	< 0.334	< 0.088	< 0.049	< 0.008
POd	< 0.038	< 0.025	< 0.023	< 0.027	< 0.334	< 0.088	< 0.049	< 0.008
PPp	< 0.038	< 0.025	< 0.023	< 0.027	210 ± 49	45 ± 2	< 0.049	< 0.008
PPy	< 0.038	< 0.025	< 0.023	< 0.027	53 ± 65	2 ± 1	< 0.049	< 0.008
PPb	< 0.038	< 0.025	< 0.023	< 0.027	442 ± 32	120 ± 34	< 0.049	< 0.008
PPo	< 0.038	< 0.025	< 0.023	< 0.027	< 0.334	< 0.088	< 0.049	< 0.008
PPpi	< 0.038	< 0.025	< 0.023	< 0.027	103 ± 23	50 ± 21	< 0.049	< 0.008
PPg	< 0.038	< 0.025	< 0.023	< 0.027	< 0.334	< 0.088	< 0.049	< 0.008

M1 = methodology 1 and M2 = methodology 2 mean ± standard deviation (n=3).

The focus of this study is on elements with known significant toxicological properties such as Ni, Pb, and As. Also, the Zn is an essential element, and at high levels may cause adverse effects on human health in cosmetic products. According

to da Costa et al. [12], Zn is an essential micronutrient and its toxicity is rare it can be easily found in facial cosmetics in the form of oxides [12], commonly employed in cosmetics for blocking ultraviolet light or coloring pigments [21].

The cosmetic samples presented Ni, Pb, and As concentration below the LOD (Table 3).

For all elements, Ni, Pb, Zn, and As, the values varied according to the methodology used in the sample digestion. In general, the smallest LOD was observed by methodology 2. The pre-digestion with H₂O₂ instead of calcination of the sample at 600°C for 2 hours is the main difference between the methodologies.

The Ni LOD obtained by FAAS according to methodology 1 and 2, were 0.038 and 0.025 µg L⁻¹, respectively. This Ni results indicate that the analytical technique has no analytical sensibility to the Ni determination in the BL, SH, PO and PP cosmetic samples analyzed in this work. Thus, it cannot be said that there is no Ni in the analyzed samples.

The results obtained by Volpe et al. [23] shown that the Ni concentrations in eye shadows from Italy, China and USA varied from 0.022 ± 0.002 to 4.25 ± 0.06 µg L⁻¹. In this study, the determination was performed by inductively coupled plasma-mass spectrometry (ICP MS).

The mean ± standard deviation values of Ni concentration in face powder and lipstick obtained by Sani et al. [11] ranges between 8.09 ± 4.79 and 8.82 ± 4.19 mg kg⁻¹ and 8.24 ± 3.29 and 5.15 ± 4.19 mg kg⁻¹, respectively. In this study, the cosmetic samples were acquired at different shopping malls and markets

in Kano Metropolis, and the samples were digested and analyzed using FAAS.

Bocca et al. [19] determined the levels of Ni and other potentially allergenic metals in Ni-tested commercial body creams by sector field inductively coupled plasma mass spectrometry (SF ICP MS). Contado et al. [24] analyzed nine cheap eye shadow products by GFAAS to quantify Ni contents.

Similar to the results obtained for Ni were observed to Pb and As. In Table 3 all the samples digested by methodology 1 and 2 presented Pb and As contents below of the LOD. The LOD to Pb by FAAS range between 0.023 and 0.027 mg L⁻¹ and to As by GFAAS range between 0.049 and 0.008 mg L⁻¹ to methodologies 1 and 2, respectively.

The Pb concentrations in eye shadows varied from 0.57 ± 0.01 to 81.50 ± 0.89 µg g⁻¹ in results obtained by Volpe et al. [23] to eye shadows from China, Italy, and USA using a FAAS. Sani et al. [11] obtained Pb concentrations in face powder between 0.13 ± 0.042 and 0.17 ± 0.12 mg kg⁻¹.

The Pb potentially affects almost every system, such as the reproductive, neurological, hematopoietic, hepatic, and renal systems in the human body. The Pb can even cause cancer due to excessive accumulation in the human body [25]. Exposure to As can cause a variety of diseases, including skin lesions, neurological and respiratory effects, atherosclerosis, and several types of cancer [26].

Hepp et al. [14] reported total amounts of As in 150 cosmetic products of 12 types sold on the USA market, and overall, cosmetic products were found to contain mean values of 0.21 mg kg^{-1} As. Jelić et al. [13] examined the presence of As in 10 samples of lipsticks and 8 samples of nail polishes, and the results show this element was very low or under the analytical methods limit in both samples.

From Table 3, Zn concentration in BL, SH, and PO presented values below of the LOD, 0.334 mg L^{-1} to methodology 1 and 0.088 mg L^{-1} to methodology 2. However, in the PPpi, Ppp, Ppy and PPb samples the Zn concentrations range between 53 ± 65 and $442 \pm 32 \text{ mg L}^{-1}$ (methodology 1), and 2 ± 1 and $120 \pm 34 \text{ mg L}^{-1}$ (methodology 2).

The high concentrations of Zn in some of the PP samples are probably due to the use of Zn oxide, an inorganic pigment [10]. The Zn oxide is a white pigment commonly employed in cosmetic formulations. The white pigments are required for skin protection during cosmetic use [27], and to block ultraviolet radiation [21]. Others substances, such as titanium dioxide can be used with the same function [27]. In PPO samples, values below the LOD may be associated with the use of another ingredient with the same function as Zn oxide. The powdered blushes do not contain much Zn oxide [28], in other words, this affirmation corroborate with the results presented in Table 3.

These results reinforce the importance of new studies about the chemical characterization of cosmetic products for children. It is more results about the qualitative and quantitative composition and that include a greater diversity of cosmetic products for children. Based on these data, new legislation could then be created to regulate the composition of products intended for application for children.

Several government and industry sources have established maximum limits for chemical elements in cosmetics. However, there is a lack of standardization between them around the world. In some cases, the limits are established based on the concentrations of elements commonly found in cosmetics sold in each country [3].

In Brazil, the Agência Nacional de Vigilância Sanitária (ANVISA) is responsible for the marketing authorization of cosmetics, and supervises and establishes standards for manufacturers, checking the production process, in addition to regularly publish a list of irregular cosmetic products [29-33]. The ANVISA also provides the national limits of chemical elements in cosmetic products. However, there is no specific legislation for children's cosmetics, such as PP.

According to the ANVISA (ANVISA, N°44/2012) [34], the maximum level of impurities allowed for artificial organic dyes in cosmetics is 3 mg kg^{-1} for As (as As_2O_3), 20 mg kg^{-1} for Pb and 100 mg kg^{-1} for other metals. The Cosmetic Products

Directive 76/768/EEC (Art.2) (EU, 1976) [35] prohibits the presence of As in all types of cosmetics, being considered a toxic element to humans. Brazil provides a national limit of $20 \mu\text{g g}^{-1}$ of Pb in eye products, lipsticks and lip pencils [34].

Most of the methods reported in the literature for elemental determination in cosmetics involve the sample preparation step and subsequent determination of elements by spectrometric techniques [3]. About the sample preparation, Sani et al. [11] used ashed samples, HNO_3 and a hot plate in the digestion of cosmetic products. Sainio et al. [15] used HNO_3 and HCl, and the samples were heated slowly in a sand bath nearly to dryness. Wang et al. [20] used a microwave assisted and HNO_3 . Others methodologies of cosmetic sample preparation are found in the literature [9, 10, 13, 19, 21-23, 36]. The diversity between the sample preparation methodologies proposed in the literature motivated in this work the comparison between two different methodologies: the methodology 1 (methodology proposed by Ullah et al. [16] with some modifications) and the methodology 2 (methodology proposed in this study).

The main differences among the methodologies are that the methodology 2 does not require a long time of sample pretreatment as methodology 1, 2 hours of calcination plus the time of cooling to room temperature. In methodology 2, the

sample pretreatment was replaced by pre-digestion with 1 mL of 35% (v v^{-1}) H_2O_2 for 1 hour. Consequently, methodology 2 allows us to digest a larger number in less time, even if it has one more step (ultrasonic bath for 30 minutes).

Another important difference among the methodologies is the volume of HNO_3 . In methodology 2 half the volume (1 mL) of methodology 1 (2 mL) is used.

In general, methodology 1 consumes more energy and acid (HNO_3), and the proposed methodology (methodology 2) is faster and cheaper, and it can be performed with instruments commonly found in laboratories.

The methodology proposed in this study (methodology 2) was compared with some methodologies applied in the cosmetic digestion [11, 20, 37]. The methodology proposed to the consumers a lower volume of reagents, generate less waste volume, does not use reagent with high hazard (HF), and employs equipment for easy acquisition and maintenance, such as ultrasonic bath and digester block.

3.2 Moisture and Ashes Content Determination

In Figure 1 are presented the moisture and ashes content in BL, SH, PO and PP samples.

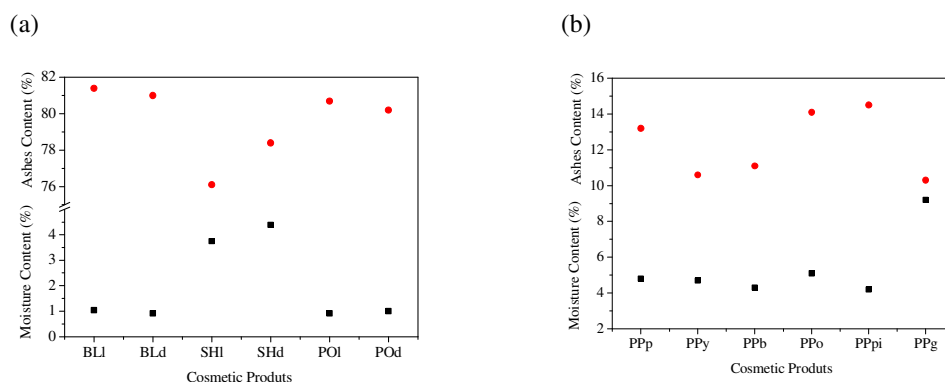


Figure 1. Moisture (■) and ashes (●) content in (a) BL, SH, and PO samples, and in (b) PP samples.

As shown in Figure 1, the moisture content varied from 0.92 to 9.20%. The highest moisture contents were observed to PP (Figure 1b). This result indicates that in general the cosmetic products, BL, SH, PO, and PP have a small amount of water in their composition.

The ashes are the residue obtained after combustion under specific conditions, and are formed by oxides resulting from the combustion of the original mineral material. Thus, the determination of the ashes content in cosmetic products can be used as an indicator of the amount of mineral salts [38].

The BL, SH, and PO presented ashes content between 71.6 to 81.4% (Figure 1a), and in the PP the ashes contents varied from 10.3 to 14.5% (Figure 1b). These results indicate that the cosmetic products, BL, SH, and PO present the highest mineral content, mainly oxides, if compare to PP samples. These results confirm that the cosmetic sample characterized have matrices with varied

compositions. According to Atz and Pozebon [39], the pigments more frequently used in cosmetics are in general oxides, such as iron oxide, chromium oxide, titanium dioxide, Zn oxide. The micas, aluminosilicates coated with titanium dioxide, iron oxide, or titanium dioxide, also are commonly used in the production of cosmetics because contain some pigments capable of producing pearly effects [40].

The SH is available in several colors, and pigments such as iron oxide, titanium dioxide, copper powder, and chromium oxide, which are commonly used in this cosmetic [39]. Moreover, substances such as titanium dioxide, bismuth oxychloride, and micas may be used to provide various effects to these products. PO usually uses iron oxides as the main pigment, but other inorganic pigments, such as ultramarines, chrome oxide, and chrome hydrate, also may be used [28]. The iron oxide is also a common dye in BL [11].

4 Conclusions

The proposed methodology consumes less energy and acid (HNO_3), is faster and cheaper, and it can be performed with instruments commonly found in laboratories.

From the results obtained, Ni, As, Zn, and Pb were not detected in the BL, SH, and PO products from China, and Ni, As, and Pb were not detected in PP from Brazil.

The application of FAAS, preceded by sample preparation using the methodologies 1 and 2, has allowed the Zn quantification in PP samples. The Zn was found at concentrations between $2 \pm 1 \text{ mg L}^{-1}$ and $442 \pm 32 \text{ mg L}^{-1}$.

It is important to avoid the use of cosmetic products by children. ANVISA recommends that kids use only children's products [41]. However, as the commercialization of cosmetic products for this public has grown in recent years, the following actions are recommended:

- (1) Regular monitoring of potentially toxic elements in PP products;
- (2) New studies about the Zn levels in cosmetic products for children;
- (3) The creation of legislation to regulate the composition of PP products.

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PRODUTOS COSMÉTICOS PARA CRIANÇAS E ADULTOS - DETERMINAÇÃO DOS TEORES DE As, Ni, Pb E Zn

RESUMO: O objetivo deste trabalho foi determinar a concentração de elementos potencialmente tóxicos em diferentes produtos cosméticos, usando metodologias de digestão simples, acessíveis e técnicas espectroscópicas. Um total de doze produtos foram selecionados, comprados e analisados, os quais incluem blush (BL), sombra para os olhos (SH), pó facial (PO) e tinta em pó para crianças (PP). As amostras foram secas (a 100°C), trituradas e homogeneizadas. Para digestão duas metodologias foram empregadas. Os teores de Ni, Pb e Zn foram quantificados

por espectrometria de absorção atômica com chama (FAAS), e os teores de As por espectrometria de absorção atômica com atomização eletrotérmica em forno de grafite (GFAAS). Em geral, as amostras apresentaram teores abaixo do limite de detecção (LOD) para Ni, Pb, As e Zn. No entanto, algumas amostras de PP apresentaram teores de Zn entre 2 ± 1 e 442 ± 32 mg L⁻¹. Esse resultado deve-se provavelmente ao uso de alguns pigmentos naturais ou inorgânicos, e sugerem as seguintes ações: (1) monitoramento regular de elementos potencialmente tóxicos em produtos de PP; (2) novos estudos sobre os níveis de Zn em produtos cosméticos para crianças; e (3) a criação de legislação para regular a composição dos produtos de PP.

Palavras-chave: Blush. Sombra. Pó compacto. Tinta em pó. Espectrometria de absorção atômica com chama. Espectrometria de absorção atômica com atomização eletrotérmica em forno de grafite.

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