Development of a simple method for the determination of lead in lipstick using alkaline solubilization and graphite furnace atomic absorption spectrometry

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ABSTRACT

A simple method was developed for determining the total lead content in lipstick samples by graphite furnace atomic absorption spectrometry (GFAAS) after treatment with tetramethylammonium hydroxide (TMAH). Multivariate optimization was used to establish the optimal conditions of sample preparation. The graphite furnace heating program was optimized through pyrolysis and atomization curves. An aliquot containing approximately 50 mg of the sample was mixed with TMAH and heated in a water bath at 60 °C for 60 min. Using Nb as the permanent modifier and Pd as the chemical modifier, the optimal temperatures were 900 °C and 1800 °C for pyrolysis and atomization, respectively. Under optimum conditions, the working range was from 1.73 to 50.0 $\mu g \, L^{-1}$, with detection and quantification limits of 0.20 and 0.34 $\mu g \, g^{-1}$, respectively. The precision was evaluated under conditions of repeatability and intermediate precision and showed standard deviations of 2.37%–4.61% and 4.93%–9.75%, respectively. The % recovery ranged from 96.2% to 109%, and no significant differences were found between the results obtained using the proposed method and the microwave decomposition method for real samples. Lead was detected in 21 tested lipstick samples; the lead content in these samples ranged from 0.27 to 4.54 $\mu g \, g^{-1}$.

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1. Introduction

Over the past years, the worldwide use of cosmetic products has been increasing at an alarming rate due to the unending pursuit for individual beautification and a sharp rise in product advertisements in electronic media. Most of these cosmetic products are directly applied to the human skin. While the skin provides a great protective barrier, some of the ingredients in cosmetic products are able to penetrate the skin and reach vital internal organs via the systemic circulation [1]. Cosmetic products that are applied to mucous membranes are even more hazardous, for example, lip products such as lipsticks. In addition to these risks, lipsticks also have a higher risk of direct oral ingestion, which can aggravate the negative effects of its chemicals [2].

Recent media reports described the presence of Pb in lipsticks and suggested that under conditions of ordinary use, the potential Pb exposure may be harmful [3–5]. It has been estimated that a woman inadvertently ingests 1.8 kg of lipstick during her lifetime [3]. It is reasonable to assume that when a woman licks her lips, eats and/or drinks while wearing lipstick, she could ingest Pb from the lipstick. When Pb accumulates in the body over time, the exposure levels and consequences may be significant. Lead may cause serious health hazards, such as both acute and chronic poisoning, pathological change of organs; it can cause diseases in the cardiovascular system, kidney, bone, and liver, and it may even cause cancer when excessive Pb accumulates in the human body [6,7]. Lead has also been linked to miscarriage and reduced fertility in both men and women. In pregnant women, lead can enter the fetal brain through the placenta [8].

Lead exposure assessments are frequently based on intake from food, water, or air. Toxic effects are usually due to long term exposure [9]. The World Health Organization (WHO) [10] estimated a range of 4.0–10 $\mu g \, day^{-1}$ total lead intake from air and water in adults. The major source of lead for non-occupationally exposed adults is food, with a range of 23–500 $\mu g \, day^{-1}$ total lead intake. Lead in lipsticks represents only a minor source of lead exposure compared to other sources of lead because the amount of lipstick applied daily is small. Nonetheless, one should not ignore the fact that lead accumulates in the body over time and that the continuous application of lead-containing lipstick can lead to significant accumulation and exposure [11].

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Lead contamination of lipsticks may originate from Pb solder or leaded paint in production equipment, or from contaminated dust [3]. Lipsticks may also be contaminated with Pb if they are manufactured with ingredients that naturally contain Pb or are produced under conditions that could introduce Pb into the ingredients. Dyes and pigments used as ingredients in lipsticks are regulated as color additives by the FDA and must undergo pre-market approval by the FDA before they may be used in any cosmetics [12]. The current regulations allow most color additives approved for cosmetic use to contain up to 20 μg Pb g^{-1} [13].

A variety of analytical techniques have been used for the determination of metals in cosmetics, such as laser induced breakdown spectroscopy (LIBS) [1], flame atomic absorption spectrometry (FAAS) [14], inductively coupled plasma mass spectrometry (ICP–MS) [12], inductively coupled plasma–optical emission spectrometry (ICP–OES) [15] and graphite furnace atomic absorption spectrometry (GFAAS) [11]. GFAAS appears to be a good alternative for the determination of trace elements, such as lead in lipsticks, because it is one of the most sensitive techniques, with limits of detection in the range of μg L^{-1}–ng L^{-1}, and it is extremely tolerant of complex matrices [16].

Complex samples such as lipsticks require conversion to a form compatible with the instrumentation to allow for simple and effective calibration [17]. In the previous works [12,14], sample preparation involves acid digestion in a microwave oven. However, acid digestion requires the use of strong acids, which is in disagreement with green chemistry principles and is usually time consuming, even when assisted by microwaves. In addition, acid digestion is subject to analyte loss and/or sample contamination [18]. In this context, sample preparation by the alkaline solubilization of samples with tetramethylammonium hydroxide (TMAH) is an interesting alternative that has been employed with success using biological samples, such as milk powder, bovine muscle, fish muscle, mussel tissue, human hair, blood and nail samples [19–21]. Usually, the alkaline solubilization is very simple and fast.

The aim of this work is the development of a simple analytical method for the determination of lead in lipsticks by GFAAS, after sample treatment with tetramethylammonium hydroxide. A multivariate optimization strategy based on a factorial and central composite design was employed. The method was validated and was employed to quantify lead in several lipstick samples.

2. Experimental

2.1. Instrumentation

A Perkin Elmer AAnalyst 400 atomic absorption spectrometer equipped with a HGA 800 graphite furnace and a AS-800 autosampler (Norwalk, CT, USA) was used in all measurements of Pb integrated absorbance. Background correction was made with a continuous light source (deuterium lamp) (Perkin Elmer, Norwalk, CT, USA). Argon (99.996%; White Martins, São Paulo, SP, Brazil) was used as the purge gas. Perkin Elmer pyrolytic graphite-coated tubes with L'vov platforms were used. A Pb hollow cathode lamp (Perkin Elmer, Norwalk, CT, USA) was used at a wavelength of 283.3 nm, a spectral bandpass of 2.7/1.05 nm and a current of 10 mA (in accordance with the manufacturer's recommended conditions).

A Milestone Ethos 900-Mega II microwave oven (FKV Milestone, Milan, Italy) with a PTFE-vessel rotor was used to digest the lipstick samples.

2.2. Reagents, materials and samples

Deionized water (resistivity of 18.2 MΩ cm^{-1}) was generated with a Direct-Q system (Millipore, Billerica, MA, USA) immediately before use for the preparation of all solutions. The alkaline solubilization was performed with tetramethylammonium hydroxide 25 w/v% in water (Sigma–Aldrich, São Paulo, Brazil). Concentrated nitric acid and hydrogen peroxide were obtained from Merck (Darmstadt, Germany). Iridium, niobium, tantalum, ruthenium, rhodium and zirconium solutions (1000 mg L^{-1}) were purchased from Fluka (Buchs, Switzerland) in 1.0 mol L^{-1} hydrochloric acid. A 1000 mg L^{-1} palladium solution was obtained from Ultra Scientific (North Kingstown, RI, USA).

Plastic bottles, autosampler cups, and glassware were all soaked in 20 v/v% HNO$_3$ for 24 h, rinsed several times with Milli-Q water, and dried at room temperature prior to use. An autosampler washing solution containing 0.05 v/v% Triton X-100 (Merck, Darmstadt, Germany) and 0.1 v/v% isopropanol (Sigma-Aldrich, São Paulo, Brazil) was used to avoid analyte adsorption onto the surface of the container and clogging of the capillary sampling tip. The stock lead solution (1000 mg L^{-1}) was prepared using lead from Titrisol Merck (Darmstadt, Germany) in a 5 v/v% nitric acid solution.

Lipstick samples of different brands and colors were acquired at the local market (Belo Horizonte, Brazil). Selected samples were from China, France, Taiwan, the USA and Brazil.

2.3. Graphite tube treatment

The graphite tubes were treated independently with 500 μg of each permanent modifier studied (Zr, Ir, Rh, Ru, Nb and Ta) by applying 25.0 μL (1000 mg L^{-1}) of each metal solution to the platforms that were then submitted to a graphite furnace heating program, as previously described [22]. This procedure was repeated 20 times.

2.4. Optimization strategies

The lipstick sample employed for optimization was previously analyzed to evaluate the analytical signal's relationship to Pb concentration. As the integrated absorbance obtained was considered satisfactory, the lipstick sample used in this step was not fortified.

To establish the optimal conditions for sample preparation, a 2^{4-1} factorial design was employed to evaluate the effect of the following variables: heating hold time (30 or 60 min), heating temperature (60 or 100 °C), sonication time (0 or 30 min) and volume of TMAH (0.50 or 1.00 mL). Based on these results, the optimal conditions were determined through a central composite design (CCD; 10 experiments, including 3 replicates in the center point), which considered the volume of TMAH and the heating time. The GFAAS analyses were carried out under the conditions recommended by the manufacturer (Table 1). The data were processed using Statistica 6.0 software.

The experiments were conducted to choose the appropriate permanent modifier for the determination of lead content in the lipstick sample. The integrated absorbance measurement and the background signal for this sample were obtained using separate graphite tubes treated with permanent modifiers (Rh, Ir, Zr, Nb,

Table 1
Graphite furnace heating program for the determination of Pb in lipstick samples.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow rate (mL min^{-1})
Drying	100	5	20	250
Drying	140	15	15	250
Pyrolysis	700	10	20	250
Atomization	1800	0	5	0 (read)
Clean	2600	1	5	250