Talanta 105 (2013) 272–277

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

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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ARTICLE INFO

Article history:
Received 26 June 2012
Received in revised form
8 September 2012
Accepted 14 September 2012
Available online 18 October 2012

Keywords:
Lead
Lipsticks
Graphite furnace
TMAH
Multivariate optimization

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 μg L^{-1}, with detection and quantification limits of 0.20 and 0.34 μg 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 μg g^{-1}.

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 μg 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 μg 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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http://dx.doi.org/10.1016/j.talanta.2012.09.021

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 premarket 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

Table 2
Evaluation of modifiers through the measurement of manufacturer's conditions.

Permanent modifier (500 μg)	Integrated absorbance	RSD (%)	Background absorption
Without modifier	0.183	3.28	0.091
Zr permanent	0.163	2.75	0.068
Rh permanent	0.193	2.09	0.041
Ru permanent	0.146	5.12	0.102
Nb permanent	0.202	1.59	0.035
Ta permanent	0.152	6.03	0.095
Ir permanent	0.139	6.56	0.082

*Manufacturer's conditions: 700 °C (PT) and 1800 °C (AT).

Ta, Ru) and Pd as a chemical modifier (co-injection of 2 μL of a 1000 mg L^{-1} solution). A tube without a permanent modifier was evaluated as well. The results using these modifiers are shown in Table 2.

The best modifiers from this analysis were chosen, and the graphite furnace heating program was optimized using pyrolysis and atomization curves (from 400 to 1100 °C and from 1500 to 2200 °C, respectively).

2.5. General procedure

Approximately 50 mg of the lipstick sample was weighed in polypropylene tubes, followed by the addition of 460 μL of a 25 w/v% TMAH solution. The mixture was placed in a 60 °C water bath for 60 min and the volume was then brought up to 10 mL with water.

2.6. Microwave-assisted acid digestion

The microwave-assisted acid digestion was used to compare its results to the results obtained from the proposed method. A mass of 300 mg of lipstick sample was weighed into PTFE-vessels. Volumes of 5.0 mL of HNO_3 and 2.0 mL of HF were added to each vessel, which were then submitted to the heating program of the microwave oven [12]. The program was as follows: the system was heated for 10 min to reach 180 °C, and this temperature was then maintained for 30 min. After cooling, the samples were quantitatively transferred into graduated flasks and diluted to 25.0 mL with high-purity deionized water. The samples were digested in triplicate.

2.7. Method validation

A study of the performance of the developed method was conducted to demonstrate that it is able to operate properly in most laboratories. The analytical performance parameters evaluated were as follows: selectivity (evaluated in terms of matrix effect), detection limit, quantification limit, linearity, sensitivity, precision and trueness. The validation process was conducted via tests using standard solutions, blanks and spiked samples with a standard. The validation of these methods was based mainly on the recommendations of the EURACHEM [23].

3. Results and discussion

3.1. Optimization of alkaline solubilization

TMAH is a strong organic base, is water soluble that results in colorless solutions with amine odor, and is capable of complexing and stabilizing volatile elements [24]. Tetramethylammonium hydroxide-based procedures provide a better alternative to conventional acid digestion due to its simplicity, satisfactory accuracy, precision and instrument performance reported in the majority of studies utilizing this technique. A reduction in sample preparation time and the long-term stability of the digests are two of the greatest advantages of this strategy [25]. Treatment with TMAH has been employed with success in the solubilization of complex samples as biodiesel, bovine muscle, fish muscle, milk, and human blood [19,20,26–28]. This is the first report of TMAH treatment applied to lipstick samples prior to their analysis; thus, it is important to optimize the variables that may affect the process of alkaline solubilization.

The optimal conditions of alkaline solubilization were evaluated using 2^{4-1} factorial design. The results of the factorial design are shown in a Pareto's chart of the estimated effects (Fig. 1). The volume of TMAH and the heating time were shown to have significant effects on the response (integrated absorbance) at the 95% confidence level. Based on these results, the effect of the volume of TMAH was negative, and the effect of heating time was positive, indicating that lower volumes of TMAH and higher heating times could produce a solution stable and homogenous enough to allow for its analysis by GFAAS. High volumes of TMAH led to a reduction of analytical signal and increased background.

Through the results of the factorial design, the volume of TMAH and the heating time were evaluated for final optimization. A response surface methodology using a central composite design (CCD) was used to determine the optimal conditions and the critical points for these variables. A range of 300–700 μL for the volume of TMAH and a range of 30–90 min for heating time were studied. The heating temperature and the sonication time showed no significant effects and were set to 60 °C and 0 min, respectively. The results of the experiments using the central composite design generated a response surface (Fig. 2). The heating time did not cause any significant effects, but the volume of TMAH greatly affected the analytical response. Thus, the optimal conditions used were a heating time of 60 min and 460 μL of TMAH 25 w/v%. Though the heating time is relatively long, there is no limitation to the number of samples that can be prepared simultaneously.

3.2. Modifiers and graphite furnace heating program

The difficulties of sample analysis arising from sample complexity may be overcome with chemical modifiers. In many cases, chemical modifiers can help predigest the matrix and simultaneously improve the sensitivity of the assay [29]. To choose the best permanent modifier, an analysis was performed in triplicate

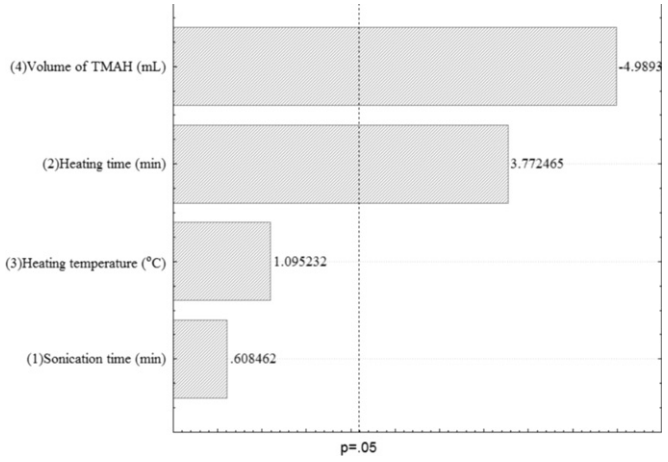

Fig. 1. Pareto chart obtained using a factorial design for the optimization of alkaline solubilization of lipsticks.

using the manufacturer's recommended conditions for drying, pyrolysis and atomization. The pyrolysis and atomization temperatures used were 700 and 1800 °C, respectively. The lipstick sample used for choosing the best permanent modifier was subjected to the previously established alkaline solubilization procedure.

The results obtained in this study are shown in Table 2. The highest analytical signal with good precision and low background signal was obtained using Nb as the permanent modifier. The use of Pd as the chemical modifier enhanced the integrated absorbance signal and was used throughout the study (Fig. 3). Dobrowolski et al. [30] studied the action of the mixed permanent modifiers Nb/Ir (niobium/iridium) and W/Ir (tungsten/iridium) for cadmium and lead determination in sediments and soils by slurry sampling graphite furnace atomic absorption spectrometry. Application of Nb/Ir modification for determination of Cd and Pb by slurry sampling GFAAS resulted in prolonged tube lifetime. It was noted that Nb/Ir is the favorable permanent modifier from the group of refractory metals for Pb and Cd determination.

After selecting the modifiers, the graphite furnace heating program was optimized through pyrolysis and atomization curves (Fig. 4). Optimal pyrolysis and atomization temperatures were determined to be 900 and 1800 °C, respectively. The atomization temperature selected for the lipstick sample was identical to that described by Baysal & Akman [31] for the determination of lead in hair (1800 °C). The value established by these authors for pyrolysis was 800 °C, which is very close to the temperature chosen for the lipstick sample in the proposed method.

3.3. Method validation

Using the optimal experimental conditions, the analytical parameters for Pb determination in lipstick samples were obtained. To verify the linearity and selectivity, three calibration curves using aqueous standard solutions with 2.5 w/v% TMAH and three matrix matching (MM) calibration curves were prepared at concentrations of 0.0, 2.5, 5.0, 12.5, 25.0, 37.5, and 50.0 μg L^{-1}. The MM curves were prepared from a lipstick that presented no analytical signal for lead when analyzed by GFAAS. Comparison of the slopes of the curves (Table 3) by means of the *F*- and the Student's *t* tests revealed significant differences at the 95% confidence level. Therefore, matrix matching calibration curves were used for calibration in all additional experiments. The homoscedasticity was confirmed by the Levene test modified [32]. The *F* test (ANOVA) was used to assess the significance of the regression and linearity deviation of the matrix matching calibration curve [33]. The linearity was confirmed in the range of 0.0 μg L^{-1}–50.0 μg L^{-1}, and the correlation coefficient was found to be 0.998. The limits of detection (LOD) and quantification (LOQ) were calculated from 10 independent blank samples (lipstick without lead) measured once each, using LOD = mean sample blank value + $3s_{blank}$ and LOQ = mean sample blank value + $6s_{blank}$, where s_{blank} is the standard deviation of the sample blanks (n = 10). The values obtained for the LOD and LOQ were 1.01 μg L^{-1} and 1.73 μg L^{-1}, respectively (which corresponds to 0.20 μg g^{-1} and 0.34 μg g^{-1}, respectively, after considering

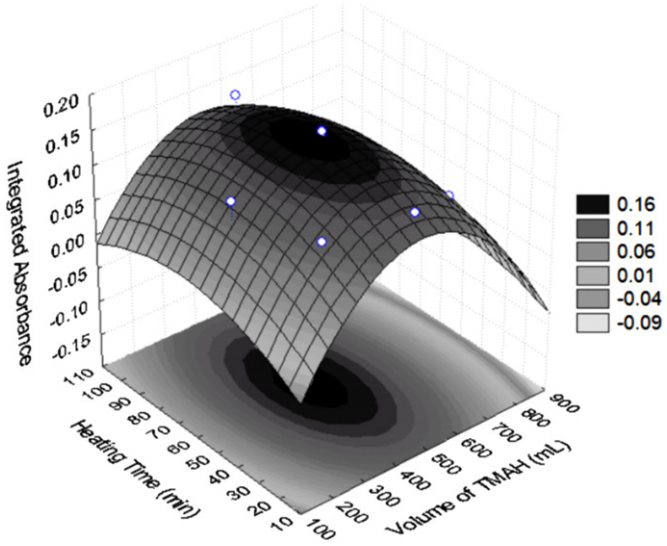

Fig. 2. Response surface obtained using a central composite design to optimize heating time and TMAH volume for alkaline solubilization of lipsticks.

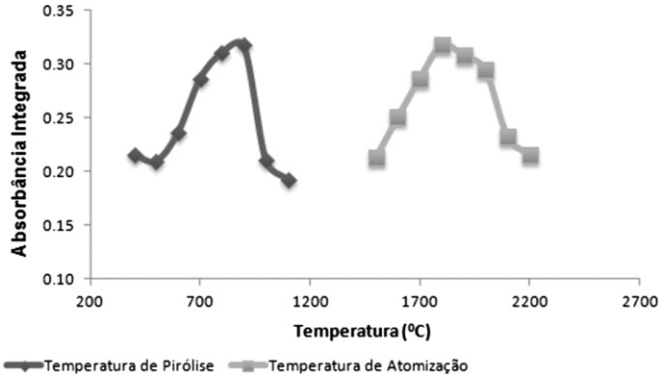

Fig. 4. Pyrolysis and atomization curves for Pb in lipstick samples treated with TMAH.

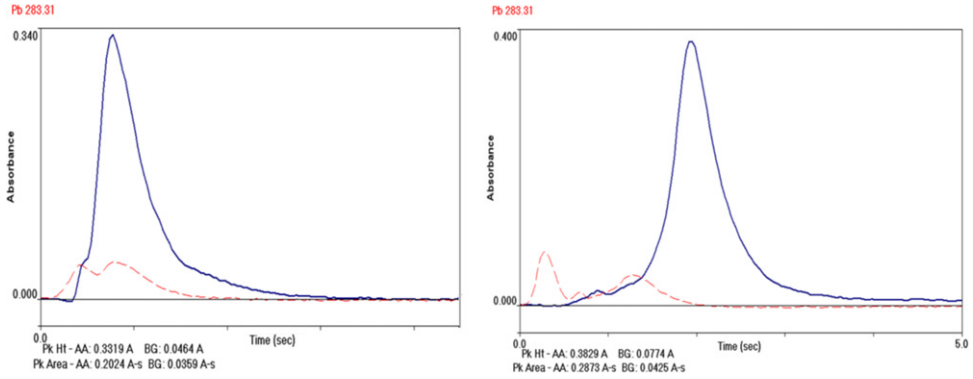

Fig. 3. Peak profile of the niobium permanent modifier (a) and niobium permanent modifier with palladium chemical modifiers (b) in lipstick samples.

Table 3
Analytical parameters of merit for the determination of Pb in lipstick samples.

Parameters	Values found
Aqueous calibration curve	$y=(0.00689\pm0.00007)x+(0.0041\pm0.0019)$
Matrix-matched calibration curve	$y=(0.00761\pm0.00008)x-(0.0042\pm0.0022)$
Working range ($\mu g\,L^{-1}$)	1.73–50.0
Characteristic mass (pg)	8.50
LOD ($\mu g\,L^{-1}$)	1.01
LOQ ($\mu g\,L^{-1}$)	1.73

sample preparation). These limits are adequate for quality control of lipsticks. The sensitivity was evaluated by calculating the characteristic mass (8.5 pg); this is less than what is specified by the manufacturer of the instrument (9.0 pg). Even with a complex matrix, the sensitivity was slightly better than expected, thus demonstrating that the proposed method for sample preparation is adequate. The precision was evaluated in terms of repeatability and intermediate precision using seven replicate blank lipstick samples spiked with three levels of Pb (2.0, 10.0 and 20.0 $\mu g\,L^{-1}$). To evaluate the repeatability, these replicates were analyzed under the same conditions within a short timescale. For the determination of intermediate precision, 21 replicates of one lipstick sample were prepared and analyzed by the same analyst using the same apparatus under the same conditions of use on an extended timescale (1 day, 1 week and 1 month; seven replicates per day). The relative standard deviation (RSD) was calculated for both the repeatability and the intermediate precision and was found to range from 2.37% to 4.61% and 4.93% to 9.75%, respectively (Table 4). This precision is adequate according to the standards of the acceptability criterion set by INMETRO [34] which establishes an acceptable relative standard deviation of up to 10% for concentrations above 100 $ng\,g^{-1}$.

Certified reference materials similar to lipsticks were not available; thus, the validity of the proposed method was checked by addition-recovery studies and by comparing the proposed method with the conventional acid digestion procedure. For the recovery study, blank samples spiked with three levels of Pb (2.0, 10.0 and 20 $\mu g\,L^{-1}$) were analyzed by the proposed method. Recovery rates between 96.2% and 109% were obtained (Table 4); these findings are considered adequate according to the acceptance criteria set by INMETRO [34] as well as the European commission [35] (which requires recoveries between 80% and 110% for concentrations above 10 $ng\,g^{-1}$). The results obtained from alkaline solubilization and the microwave-assisted digestion procedure (Table 5) were compared using the Paired *t* test. The results obtained by both procedures were in agreement at the 95% confidence level.

Thus, the results of the performance parameters studied confirmed quality assurance when using the proposed method for the analysis of Pb in lipsticks.

3.4. Lead determination in lipstick samples

The lead concentration in 22 different brands and colors of lipstick samples from several different manufacturers/countries was determined by the proposed method (Table 6). The concentrations ranged from 0.27 to 2.36 $\mu g\,g^{-1}$ for the beige colored lipsticks, 1.02 to 3.37 $\mu g\,g^{-1}$ for rose colored, 1.62 to 4.54 $\mu g\,g^{-1}$ for red colored and 1.46 to 3.72 $\mu g\,g^{-1}$ for brown colored. Comparison of the lead content according to lipstick color revealed that the highest lead content was found in red and brown lipsticks. The samples with the highest Pb content found were from lipsticks imported from China, with lead levels ranging from 2.07 to 4.54 $\mu g\,g^{-1}$.

Table 4
Precision and trueness obtained by proposed method to determine Pb in lipsticks by alkaline solubilization and GFAAS.

Spiked concentration ($\mu g\,L^{-1}$)	Repeatability (RSD, %)	Intermediate precision (RSD, %)	Recovery (%)
2.0	4.61	9.75	109
10.0	2.37	7.24	96.2
20.0	2.54	4.93	98.9

Table 5
Mean and standard deviation values ($n=3$) for Pb content of lipstick samples obtained by alkaline solubilization with tetramethylammonium hydroxide and microwave-assisted acid digestion.

Samples	Alkaline solubilization Concentration ($\mu g\,g^{-1}$)	Digestion procedure Concentration ($\mu g\,g^{-1}$)
Beige colors	2.07 ± 0.03	2.15 ± 0.08
Rose colors	3.40 ± 0.09	3.25 ± 0.10
Red colors	4.20 ± 0.07	4.32 ± 0.20
Brown colors	3.72 ± 0.06	3.56 ± 0.15

Table 6
Lead concentration (mean ± SD) in lipstick samples.

Sample	Origin country	Color	Pb ($\mu g\,g^{-1}$)
1	China	Beige creamy	2.07 ± 0.06
2	China	Beige shimmering	2.36 ± 0.07
3	China	Rose shimmering	3.37 ± 0.13
4	China	Red creamy	4.17 ± 0.10
5	China	Red shimmering	4.54 ± 0.05
6	China	Brown creamy	3.18 ± 0.02
7	China	Brown shimmering	3.72 ± 0.10
8	Brazil	Beige creamy	0.49 ± 0.05
9	Brazil	Beige creamy	0.64 ± 0.05
10	Brazil	Beige shimmering	0.62 ± 0.16
11	Brazil	Beige shimmering	0.57 ± 0.02
12	Brazil	Rose creamy	1.02 ± 0.02
13	Brazil	Rose shimmering	1.96 ± 0.05
14	Brazil	Red creamy	1.88 ± 0.09
15	Brazil	Red creamy	1.62 ± 0.05
16	Brazil	Red shimmering	1.72 ± 0.12
17	Brazil	Brown creamy	1.52 ± 0.05
18	Brazil	Brown shimmering	1.46 ± 0.09
19	Taiwan	Red shimmering	3.64 ± 0.13
20	USA	Beige creamy	0.51 ± 0.10
21	USA	Beige shimmering	0.27 ± 0.05
22	France	Rose shimmering	< LOD

Lead content was determined in 21 tested lipstick samples; the highest Pb content was 4.54 $\mu g\,g^{-1}$, and the lowest was 0.27 $\mu g\,g^{-1}$. This large variation in the concentration of lead may be attributed to the quality of the raw materials used in the production of the lipsticks. The FDA has established 20 $\mu g\,g^{-1}$ as the maximum amount of lead allowed in color additives used to make cosmetics for external use, produced using good

manufacturing practices [36]. However, there exists no legislation for regulating the level of toxic metals in lipsticks in the US, Europe, Asia or Brazil. Recently, the level of lead in a number of different lipsticks was determined by the US FDA [13]; the highest lead content found was 3.06 $\mu g\ g^{-1}$, and the lowest lead content was 0.09 $\mu g\ g^{-1}$. In 2007, lead was also found in 61% of the 33 brands of lipsticks tested by the CSC, with lead levels ranging from 0.03 to 0.65 $\mu g\ g^{-1}$ [3].

Although the lead found in lipsticks is only a minor source of lead exposure when compared to other sources such as water, food and/or air, lead exposure from lipsticks should not be overlooked. Some of the ingredients in lipsticks can penetrate the skin and reach vital internal organs via the systemic circulation. In addition, lipsticks also have a higher risk of direct oral ingestion which may aggravate the negative effects of its chemicals [2]. Metals accumulate in the body over time, and the repetitive application of metal-containing product(s) may lead to significant and dangerous levels of exposure. The effects of toxic lead exposure are well known and include damage to the kidneys and to the central nervous system, memory loss, and other symptoms [37].

4. Conclusions

A simple and fast analytical method for the determination of lead content in lipstick samples by GFAAS after alkaline treatment with TMAH has been proposed and validated. Alkaline solubilization avoids sample contamination and analyte loss because no acid digestion is required. Multivariate optimization was adequate for obtaining the optimal conditions for sample preparation. The graphite furnace heating program was optimized through pyrolysis and atomization curves. Under these conditions, the trueness, precision, and sensitivity of the method were adequate to quantify trace concentrations of Pb in lipsticks. The analyte concentrations found in the commercial samples were especially high for red and brown lipstick brands imported from China. These results confirm the importance of quality control in the production of cosmetics as well as the applicability of the proposed method.

Acknowledgments

The authors are grateful to the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG – CEX-PPM-00433-10) and the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for financial support. The A.R.S. is thankful to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) for its fellowship.

References

[1] M.A. Gondal, Z.S. Seddigi, M.M. Nasr, B. Gondal, J. Hazard. Mater. 175 (2010) 726–732.
[2] C.C. Wang, A.N. Masi, L. Fernández, Talanta 75 (2008) 135–140.
[3] Campaign for Safe Cosmetics, A Poison Kiss: The Problem of Lead in Lipstick, 2007. Available from: 〈http://www.safecosmetics.org/about/reports.cfm〉.
[4] Dangerous Levels of Lead in Lipstick, Lip Gloss?, 2006. Available from: 〈www.healthy-communications.com/6lipstickdangers.htm〉.
[5] Is Lead Inside Lipstick, 2006. Available from: 〈http://www.wpxi.com/news/news/is-lead-inside-lipstick/nGkgh/〉.
[6] K. Shrivas, K.D. Patel, J. Hazard. Mater. 176 (2010) 414–417.
[7] K. Koller, T. Brown, A. Spurgeon, L. Levy, Environ. Health Perspect. 112 (2004) 987–994.
[8] C. Basheer, S.H. Tan, H.K. Lee, J. Chromatogr. A 1213 (2008) 14–18.
[9] E. Carr, M. Lee, K. Marin, C. Holder, M. Hoyer, M. Pedde, R. Cook, J. Touma, Atmos. Environ. 45 (2011) 5795–5804.
[10] WHO, World Health Organization, Lead in Drinking-water, World Health Organization, Geneva, 2011.
[11] I. Al-Saleh, S. Al-Enazi, N. Shinwari, Regul. Toxicol. Pharmacol. 54 (2009) 105–113.
[12] N.M. Hepp, W.R. Mindak, J. Cheng, J. Cosmet. Sci. 60 (2009) 405–414.
[13] Code of Federal Regulations (2008) Title 21 (U.S. Government Printing Office, Washington, DC), Sections 73, 74, and 82.
[14] M.G. Volpe, M. Nazzaro, R. Coppola, F. Rapuano, R.P. Aquino, Microchem. J. 101 (2012) 65–69.
[15] K.D. Besecker, C.B. Rhoades, B.T. Jones, Atom. Spectros. 19 (1998) 48–54.
[16] I.C.F. Damin, M.B. Dessuy, T.S. Castilhos, M.M. Silva, M.G.R. Vale, B. Welz, D.A. Katskov, Spectrochim. Acta Part B 64 (2009) 530–536.
[17] E.S. Chaves, F.G. Lepri, J.S.A. Silva, A.J. Curtius, J. Environ. Monit. 10 (2008) 1211–1216.
[18] M.A. Vieira, L.C.C. Oliveira, R.A. Gonçalves, V. Souza, R.C. Campos, Energy Fuel 23 (2009) 5942–5946.
[19] D.P. Torres, V.L.A. Frescura, A.J. Curtius, Microchem. J. 93 (2009) 206–210.
[20] J.L. Rodrigues, D.P. Torres, V.C.O. Souza, B.L. Batista, S.S. Souza, A.J. Curtius, F. Barbosa Jr, J. Anal. At. Spectrom. 24 (2009) 1414–1420.
[21] B.L. Batista, J.L. Rodrigues, J.A. Nunes, L. Tormen, A.J. Curtius, F. Barbosa Jr., Talanta 76 (2008) 575–579.
[22] J.B.B. Silva, M.A.M. Silva, A.J. Curtius, B. Welz, J. Anal. At. Spectrom. 14 (1999) 1737–1742.
[23] EURACHEM, The Fitness for Purpose of Analytical Methods: A Laboratory Guide to Method Validation and Related Topics, LGC, Teddington, UK, 1998.
[24] M. Ghisi, A.S. Ribeiro, M.A. Vieira, A.J. Curtius, Rev. Analytica 28 (2007) 58–65.
[25] J.A. Nóbrega, M.C. Santos, R.A. Sousa, S. Cadore, R.M. Barnes, M. Tatro, Spectrochim. Acta Part B 61 (2006) 465–495.
[26] M. Ghisi, E.S. Chaves, D.P.C. Quadros, E.P. Marques, A.J. Curtius, A.L.B. Marques, Microchem. J. 98 (2011) 62–65.
[27] Y. Wu, Y.I. Lee, L. Wu, X.D. Hou, Microchem. J. 103 (2012) 105–109.
[28] A.S. Ribeiro, A.L. Moretto, M.A.Z. Arruda, S. Cadore, Microchim. Acta 141 (2003) 149–155.
[29] F.R. Amorim, M.B. Franco, C.C. Nascentes, J.B.B. Silva, Food Anal. Meth 4 (2011) 41–48.
[30] R. Dobrowolski, A. Adamczyk, M. Otto, Talanta 82 (2010) 1325–1331.
[31] A. Baysal, S. Akman, Spectrochim. Acta Part B 65 (2010) 340–344.
[32] S.V.C. Souza, R.G. Junqueira, Anal. Chim. Acta 552 (2005) 25–35.
[33] D.A. Belsley, E. Kuh, R.E. Welsch, Regression diagnostics: identifying influential data and sources of collinearity, Wiley, New York, 1980.
[34] INMETRO, Instituto Nacional de Metrologia, Normalização e Qualidade, Orientação sobre Validação de Métodos Analíticos, 3ª revisão, Brasil, fevereiro de 2010.
[35] European Commission. Commission decision 2002/657/EC of 12 August 2002. Implementing Council Directive 96/23/EC Concerning Performance of Analytical Methods and the Interpretation of Results. Official Journal of the European Communities, L 221/8, 2002.
[36] US FDA.United States Food and Drug Authorities, 2002a. Title 21 – Food and Drugs. Chapter I – Food and Drug Administration, Department of Health and Human Services. Part 74 – Listing of Color Additives Subject to Certification/ Office of Cosmetics and Colors. Sec. 74.1306 D&C Red No. 6. Available from: 〈http://www.cfsan.fda.gov/lrd/cf741306.html〉.
[37] M. Ahamed, K.J. Siddiqui, Clin. Nutr. 26 (2007) 400–408.