Article

Rapid Determination of Lead in Progressive Hair Dye Lotion by Spot Test/Diffuse Reflectance Spectroscopy with a Paper Platform

Vitor H. M. Luiz, Lívia M. Saraiva, Ângela P. Martins, Leonardo Pezza and Helena R. Pezza*

Instituto de Química, Universidade Estadual Paulista - UNESP, Rua Prof. Francisco Degni 55, CP 355, 14800-900 Araraquara-SP, Brazil

A simple, inexpensive, and clean methodology employing a combined spot test/diffuse reflectance spectroscopy procedure was developed and applied for the quality control analysis of lead in hair dyes, using a filter paper platform. The method is based on the complexation reaction of lead, present in a pH 2.8 buffer medium containing tartaric acid and sodium and potassium tartrate, with sodium rhodizonate (ROD) in an aqueous medium containing sodium dodecyl sulfate (SDS) surfactant, yielding a colored compound on the surface of a filter paper. The concentrations of ROD and SDS were optimized using experimental design. The linear range obtained for reflectometric measurements carried out at 545 nm was 4.70-140 mg L^{-1} of lead (R = 0.998), and the limits of detection and quantification were 1.12 and 3.75 mg L^{-1}, respectively. The proposed method was successfully applied to the analysis of lead in progressive hair dyes.

Keywords: lead, progressive hair dye, spot test, diffuse reflectance spectroscopy

Introduction

Lead is neither essential nor beneficial to plants and animals. It is one of the most common elements toxic to mammals and can cause mental retardation in young children. Tests with rats and mice have shown that the chemical and toxicological properties of inorganic lead salts, where the bond between the metal and the ligand is ionic, are different to those of covalently bonded organolead compounds. The kidney is the principal organ affected by lead salts, regardless of the route of exposure.[1-3]

Most methods for the determination of lead employ atomic absorption spectrometry[4-7] or voltammetry,[8-11] although fluorescence spectroscopy[12] and potentiometry have also been used.[13] These techniques have been applied to matrices including water,[6,7] urine,[4] gunshot residues,[9] food,[12] blood,[13] and cosmetics.[14]

The use of cosmetics is not a recent practice. Hair dyes and other kinds of cosmetics have been used since the times of the ancient Egyptians and the Roman Empire.[14] However, with the development of new products that are accessible and easy to use, there is increasing use of cosmetics. These products enter into direct contact with the hair, skin, mouth, or other parts of the human body. Since the skin does not

provide an impermeable barrier to many topically applied substances,[15] it is important to determine the maximum permissible concentrations of potentially toxic substances, in order to avoid any harm to the users.

Given the chemical nature of hair dye ingredients and the size of the exposed population, hair dyes are among the most extensively studied and regulated cosmetic products, and their use has been included in the investigation of endpoints in numerous epidemiological studies.[15]

One of the elements of interest present in progressive hair dyes is lead, found as lead acetate and used as a color additive. Lead acetate is approved by the United States Food and Drug Administration (FDA)[16] and the Brazilian National Health Surveillance Agency (ANVISA)[17] as an additive for coloring hair on the scalp, at concentrations not exceeding 0.6% (m/v) of metallic lead.

Combined spot test/diffuse reflectance spectroscopy using filter paper offers advantages over other methods, including simplicity and extremely low consumption of reagents and solvents. The technique is therefore attractive for the development of analytical methods that comply with the principles of Green Chemistry, which aims to develop techniques that reduce or eliminate the use and generation of substances hazardous to human health or to the environment.

Spot test reactions have been successfully used in several applications including large-scale clinical, environmental,

*e-mail: hrpezza@iq.unesp.br

food, and water analyses.[18,19] Spot tests are performed by mixing a drop of the sample and a drop of a specific reagent on a porous support. A filter paper impregnated with a stable reagent is the most common configuration for spot tests used in clinical and water quality analyses.[19]

Filter papers are used as platforms in analytical and clinical applications[20-22] because they can be readily disposed of safely by incineration.[23] Whitesides and co-workers[24] developed patterned paper-based microfluidic systems for biodetection. Colorimetric paper platforms can be used without any instrumentation or trained personal, with samples delivered by spotting. A white filter paper provides a good surface for spot tests, ensuring a high contrast background for colorimetric reactions that are measured by reflectance.[23,25-27]

Reflectance takes place when light strikes a surface. Two distinct processes are responsible for this, namely specular reflectance and diffuse reflectance. Specular reflectance occurs at the interface of a medium with no transmission through it, while diffuse reflectance occurs when the radiation penetrates the material surface and subsequently reappears on the surface after undergoing partial absorption and multiple scattering within the internal layer. Specular reflection can be eliminated or minimized by means of optical engineering, with use of spherical or 45° illumination systems. Specular reflectance is not of importance in the field of colorimetry.[28] In contrast, diffuse reflectance has a broad range of applications, using materials with irregular surfaces, such as paper, as solid supports. Scheme 1 shows these two kinds of reflectance and the process that occurs when the incident radiation strikes the spot test.
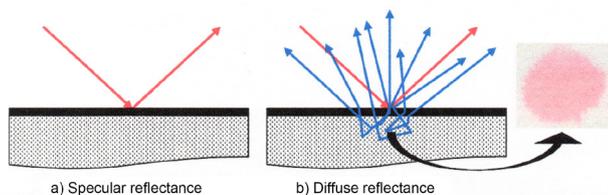
Scheme 1. Two kinds of surface reflection: a) specular reflection produced by a mirror; b) diffuse reflection after a light beam strikes a spot test on a paper platform.

Diffuse reflectance measurements can be performed *in situ* using a very simple homemade reflectometer[29] or a portable diffuse reflectance spectrophotometer.[23,26] Alternatively the analyte of interest can be collected on the filter paper and retrieved to the laboratory, under appropriate storage conditions, for subsequent analysis. It is also possible to photograph the result of the *in situ* reaction and send the image to an analyst by e-mail or cell phone.[30]

The required instrumentation is small, lightweight, inexpensive, and can be battery operated. These characteristics make the method highly attractive for use in many applications, in almost any location, by nearly everyone.[25] Previous studies have demonstrated that diffuse reflectance spectroscopy can yield reliable results and that the technique is suitable for quantitative analysis. Several analytical applications have been reported for different kinds of matrices and analytes.[23,25-27,29-34]

Diffuse reflectance is known to be dependent on the composition of the system, analogous to light absorption. Therefore, reflectance studies can be used for quantitative chemical analysis in much the same way that transmission spectrometry is used. In reflectance analysis, the optical density for reflectance measurements is $A_R = -\log T_R$, analogous to absorbance, where $T_R = I/I_0$ is the reflecting power, I_0 being the intensity of the incident radiant energy and I the intensity of the radiant energy reflected by the medium.[33,34]

This paper describes the development and application of a simple, portable, and environmentally friendly method for the rapid determination of lead in progressive hair dye products. The proposed method is based on diffuse reflectance measurements of the colored product (λ_{max} = 545 nm) produced from the spot test reaction between lead and sodium rhodizonate in a buffer medium of tartaric acid and sodium and potassium tartrate at pH 2.8, using a filter paper as the platform.

Experimental

Apparatus

Reflectance measurements were made using a handheld integrating sphere (ISP-REF, Ocean Optics) connected to a fiber optic mini-spectrometer (USB2000, Ocean Optics). The USB2000 mini-spectrometer was fitted with a 2048 pixels Sony ILX511 CCD array detector. The SpectraSuite and OOIBase 32 software packages (Ocean Optics) were used for acquisition and processing of the spectra. Measurements of pH were made with a Tec-2 pH meter (Tecnal) equipped with a glass electrode. Eppendorf (10-100 μL) and Brand (100-1000 μL) micropipettes were used to deliver measured volumes in the experiments. Grade "A" glassware was employed in all the procedures. Weighing was performed with a Mettler Toledo model AG204 analytical balance. The analyte was separated from the samples using an Eppendorf 5702R centrifuge. Samples were evaporated using a Marconi MA 126 water bath, and a Corning magnetic stirrer was used for agitation. In the comparative method, samples were calcined in a Marconi MA 385 muffle furnace.

Reagents and solutions

Whatman No. 1 qualitative filter paper was used as the solid support. All the reagents employed were analytical grade and were used without any prior purification. Ultrapure water (18 MΩ cm, Milli-Q system, Millipore) was used to prepare the solutions.

The chromogenic reagent solution consisted of a mixture of sodium rhodizonate (ROD, Sigma-Aldrich, 97%) and sodium dodecyl sulfate (SDS, Sigma, 99%) at concentrations of 13 mmol L^{-1} and 9.0 mmol L^{-1}, respectively, in pH 2.8 buffer medium containing sodium and potassium tartrate (Synth, 99%) and tartaric acid (Synth, 99%), both at 0.2 mol L^{-1}.

A stock standard solution of 2000 mg L^{-1} of lead(II) ($(Pb(NO_3)_2$, Sigma-Aldrich, purity > 99.0%) was prepared once. Working solutions of lead (4.70, 9.40, 18.75, 37.50, 65.60, 93.70, and 140 mg L^{-1}) were prepared by appropriate dilution of the stock solution with deionized water. Nitric acid (HNO_3, Quimex, 65% m/m) and sulfuric acid (H_2SO_4, Sigma-Aldrich, 98% m/m) were used for sample digestion.

Samples and preparation

Four progressive hair dye lotions were obtained from supermarkets in Brazil. The samples solutions were prepared by dilution of 1.0 mL of each lotion up to 25 mL with deionized water in volumetric flask. This dilution was stipulated after preliminary tests. Samples with higher lead content require appropriate dilution. In the case of the reference method, sample preparation was performed according to the procedure established by ANVISA.[35]

Experimental design

The significant parameters were evaluated by means of experimental design methodology. The selected variables were the concentrations of ROD and SDS. These multivariate analyses were performed with the Minitab 16 and Statistica v. 8.0 software packages.

Spot test - recommended procedure

For the spot test reaction, the solutions were spotted onto 2.25 cm² filter papers (Whatman No. 1). The chromogenic reagent solution (20 µL) was added first, immediately followed by 20 µL of the lead solution. The solutions were spotted onto the center of the filter paper using a micropipette fixed in a holder, according to the procedure described by Tubino *et al.*[27] The reflectance was then measured at 545 nm. The blank was prepared using 20 µL of the chromogenic reagent solution and 20 µL of deionized water.

Stability study

The stability of the colored reaction product in the filter paper was evaluated by kinetic monitoring of the absorbance signal at 545 nm, with measurements every five minutes during one hour.

Evaluation of interferences

This study employed solutions containing 0.6% (m/v) of lead, together with each of the other hair lotion ingredients (propylene glycol, ammonium chloride, panthenol, acetic acid, and benzoate), used separately at concentrations equal to the lead concentration. After mixing, 1 mL of each solution was diluted in a 250 mL volumetric flask with deionized water. The analysis was carried out as described in the recommended procedure.

Analytical curves

Under optimized conditions, lead standard solutions (from 4.70 to 140.0 mg L^{-1}) were reacted in triplicate with the reagent, using the filter paper as solid support. Formation of the colored product was monitored at 545 nm.

Proposed method

The determination of lead was performed using four samples of progressive hair dye lotion, considering the maximum limit allowed by ANVISA[17] (0.6% m/v of lead).

The samples were diluted in deionized water as described in the Samples and preparation section, followed by the spot test. The measurements were made at 545 nm by coupling an integrating sphere to a portable spectrophotometer.

Reference method

The gravimetric method was performed as described by ANVISA,[35] with each sample analyzed in triplicate.

Results and Discussion

An aqueous solution of sodium rhodizonate produces colored precipitates from neutral or slightly acidic lead solutions (Scheme 2). The sodium rhodizonate test meets the requirements for the highly selective detection and quantification of lead, with adjustment of pH leading to

the formation of a colored reaction product in a spot test conducted on a qualitative filter paper. This chromogenic reagent has been used previously in forensic spot testing for lead in firearm discharge residues.[19]
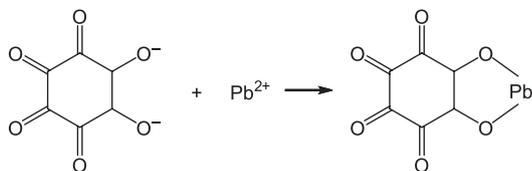
Scheme 2. Reaction between sodium rhodizonate and Pb^{2+} ions.

It is known that micellar media are capable of changing the equilibrium, kinetic, and spectral properties of reactions in which they are involved, and this has been used to improve the characteristics of analytical procedures.[36] However, there have been no previous reports concerning the use of micelles in the complexation of lead with rhodizonate.

The experiments showed that there was a significant enhancement of solubility in the presence of SDS, with increased sensitivity of the method and no shift in the absorbance maximum ($\lambda = 545$ nm). No precipitation was observed when lead was reacted with rhodizonate in the presence of SDS.

The uniformity and intensity achieved using spot tests with reflectance measurements is influenced by various experimental parameters. Here, the order of addition of the reagents was studied, together with tests to determine any need to adjust the pH of the medium. It was found that when 20 µL of the chromogenic reagent (ROD and SDS) was added to the filter paper before 20 µL of lead solution, there was a better signal and greater homogeneity of the spot, with no need to dry the reaction mixture on the filter paper.

No change in the uniformity of the colored spot was observed when different volumes of the solutions were added to the paper. In view of this, it was decided to add 20 µL of the chromogenic reagent solution followed by 20 µL of lead solution, which produced a spot of sufficient diameter to be measured by the reflectometer. In terms of the stability of the colored product over time, no significant change in the optical signal was observed for at least 60 minutes.

Optimization of variables

After identification of the significant parameters, the variables were optimized using a central composite design[37] in order to obtain the best analytical conditions for the spot reaction on the filter paper. All experimental

designs were carried out with the lead concentration fixed at 250 mg L⁻¹. The statistical calculations were performed using Statistica 6.0 software.

The factors studied were the ROD and SDS concentrations. The values of the variables were studied using five levels, with four central points. The points of a central composite design are coded unities distant from the central point (which is coded as zero); all the points therefore lie on a circumference with radius. The variables and their levels (non-coded and coded) used in the central composite design matrix are shown in Table 1. The repeatability of the method was determined by carrying out the experiment corresponding to the central point using extra replicates (four) in the center in order to estimate the experimental error.

Table 1. Matrix obtained from the coordinates of the central composite design points

Experiment	Factor	
	SDS / (mmol L⁻¹)ᵃ	ROD / % (m/v)ᵃ
1	5.73 (−)	0.129 (−)
2	9.27 (+)	0.129 (−)
3	5.73 (−)	0.271 (+)
4	9.27 (+)	0.271 (+)
5	5.00 (−)	0.200 (0)
6	10.0 (+)	0.200 (0)
7	7.50 (0)	0.100 (−)
8	7.50 (0)	0.300 (+)
9	7.50 (0)	0.200 (0)
10	7.50 (0)	0.200 (0)
11	7.50 (0)	0.200 (0)
12	7.50 (0)	0.200 (0)

ᵃThe coded values are within parentheses.

Figure 1 shows the three-dimensional response surface graph obtained from the fitting of the experimental data.

The quadratic regression model could be described by: $z = -0.083 + 0.082[SDS] - 0.007[SDS]^2 + 2.714[ROD] - 7.125[ROD]^2 + 0.154[ROD][SDS]$, where z is the response factor corresponding to the absorbance (optical density for reflectance measurements) value.

The response surface graph shows a darker region representing higher values of absorbance, indicative of the optimum conditions for the reaction to take place. After application of the statistical treatments, the best concentrations found were 0.28% (m/v) for ROD and 9 mmol L⁻¹ for SDS.

Determination of the figures of merit

The proposed method was validated by considering the linear dynamic range, repeatability, limit of detection
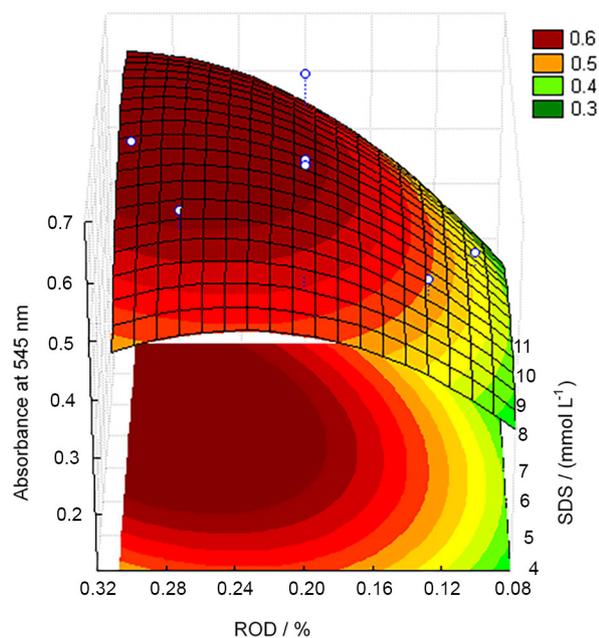
Figure 1. Optimized response surface for the measurements of absorbance at 545 nm as a function of the concentrations of ROD and SDS.

(LOD), limit of quantification (LOQ), precision, and recovery.

The analytical curve (Figure 2) was constructed in the concentration range from 4.70 to 140.0 mg L^{-1} (2.27×10^{-5} to 6.74×10^{-4} mol L^{-1}), by appropriate dilution of a stock solution of lead(II). The regression equation obtained was: Absorbance = $0.00407[Pb^{2+}] - 0.00511$ (R = 0.998). Statistical analysis was performed as described by Harris.[38]

The LOD and LOQ were determined according to IUPAC recommendations:[39] LOD = $3(\sigma/S)$ and LOQ = $10(\sigma/S)$, where σ is the standard deviation of measurements of the blank (n = 10) and S is the slope of the linear dynamic range. The LOD and LOQ were 1.12 and 3.75 mg L^{-1}, respectively.

The precision of the method, expressed as the relative standard deviation (RSD) of the response, was assessed by repetition of points of the analytical curve at different times
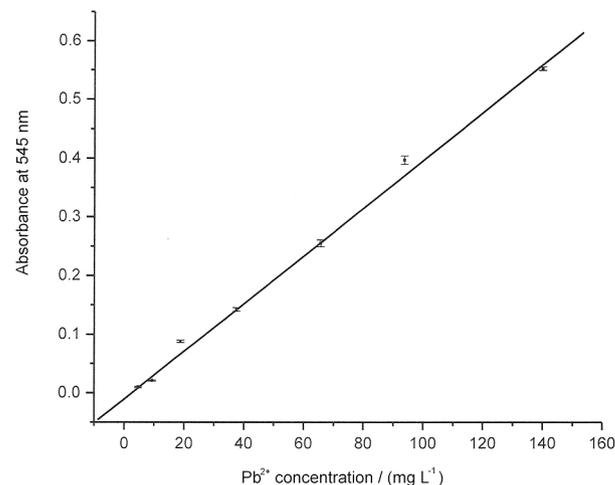

Figure 2. Analytical curve for Pb^{II}.

on one day (intra-day) and on different days (inter-day). The coefficients of variation obtained were 1.1% and 2.4%, respectively.

Compared to previously reported methods for the determination of lead in cosmetic products for changing the color of hair[14] and another matrices,[4-6,9,12,40-43] the proposed method provides lower sensitivity (higher detection limit). Nevertheless, considering the quantities of lead present in the samples studied, the proposed method is sufficiently sensitive to permit the determination of this analyte in commercial products. Table 2 shows a comparison of the analytical features of the proposed method with those achieved in previous methods described in the literature for the determination of lead in cosmetic products used to change the color of hair.

Study of interferences

Investigation was made of the effects of the common ingredients present together with lead acetate in commercial hair dye formulations (propylene glycol, ammonium chloride, panthenol, acetic acid, and benzoate). No

Table 2. Comparison of analytical parameters of methods for the determination of lead in cosmetic products used to change the color of hair

Analytical parameter	GF-AAS[a]	DRS[b]
Linear range	1.50-50.0 µg L^{-1}	4.70-140 mg L^{-1}
LOD	0.33-0.44 µg L^{-1} (depending on the sample)	1.12 mg L^{-1}
Remarks	Direct analysis without prior digestion; dilution with 2.5% (v/v) HNO$_3$ and 1.5% (v/v) H$_2$O$_2$ is required; without pre-concentration.	Sample preparation involves dilution with water without pre-concentration; no sophisticated instrumentation; rapid response time, less expensive, use of small volumes of reagents, and a single filter paper platform.
Samples	Liquid, dust, and cream hair dyes	Progressive hair lotion
Reference	14	Proposed method

[a]Graphite furnace atomic absorption spectrometry; [b]diffuse reflectance spectroscopy; LOD: limit of detection.

interferences were observed, with the signals showing differences that were less than 3%.

Application

The proposed method was applied using four samples of progressive hair dye lotion. The results obtained by the new method were compared statistically (using the paired *t*-test at a 95% confidence level) with those obtained using the reference method,[35] and showed good agreement (Table 3).

Table 3. Results for the determination of lead(II) in progressive hair lotion samples

Sample	Proposed method Pb^{2+} / % (m/v)	Reference method[35] Pb^{2+} / % (m/v)	*t*-test[a]
1	0.061 ± 0.001	0.061 ± 0.001	0.163
2	0.059 ± 0.005	0.062 ± 0.002	0.678
3	0.100 ± 0.002	0.099 ± 0.002	0.853
4	0.252 ± 0.002	0.254 ± 0.004	1.35

[a]Critical value at the 95% confidence level used was 4.303.

The calculated *t*-values did not exceed the critical values, indicating that there was no significant difference between the two methods, in terms of precision and accuracy. The Pb^{2+} concentrations measured in the progressive hair dye samples were lower than 0.6% (m/v), and were therefore in compliance with Brazilian legislation.

Conclusions

A micellar SDS medium was used in development of a diffuse reflectance spectroscopy method that showed good sensitivity, compared to other reported methods employing the same technique for quantitative determination of cations.[27,33,34] The proposed method for the analysis of lead by diffuse reflectance spectroscopy has the advantages of fast reaction and measurement, simplicity, low reagent consumption, minimal waste generation, relatively low cost, and good precision and reliability. A further benefit is that, unlike many other methods, no sample pretreatment is required (except dilution). This environmentally friendly technique was successfully applied for the determination of lead in samples of progressive hair dye lotion.

Acknowledgements

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