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A paper platform for colorimetric determination of aluminum hydrochloride in antiperspirant samples

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ABSTRACT

A simple, fast, low-cost, portable, and eco-friendly method using a spot test on a paper platform, together with diffuse reflectance spectroscopy, was developed and validated for the quantification of aluminum hydrochloride, a potential neurotoxic agent, in antiperspirant samples. The determination of aluminum hydrochloride was performed at a wavelength of 615 nm, by measuring consumption of the purple colorimetric reagent Alizarin S, due to reaction with aluminum. The linear range was from 10.0 to 125.0 mg L^{-1} and could be described by the equation: $A_R = 0.4479 - 0.002543\ C_{Al}$ ($R = 0.999$). The limits of detection (LOD) and quantification (LOQ) were 3.06 and 10.2 mg L^{-1}, respectively. The method was specific, accurate, and repeatable, with relative standard deviation (RSD) <5.0%. The recovery was between 92.2 and 103.4%. The method was successfully used for the determination of aluminum hydrochloride in commercial antiperspirant samples, revealing concentrations below the maximum permitted by current legislation.

1. Introduction

Personal hygiene has become a part of the daily routine worldwide, reflecting the concern of individuals about their welfare. Personal hygiene products such as antiperspirants and deodorants are considered indispensable, because they are no longer merely a way to maintain a sensation of cleanliness, but also contain components that treat and beautify the skin, such as vitamin E [1, 2].

Perspiration is a fundamental physiological process whose function is to control and maintain the body temperature at around 37 °C [3]. There are three different ways to reduce or control underarm odor: minimization or elimination of the secretions from both types of sweat glands; prevention of bacterial growth; and absorption of body odors. For these purposes, two different product categories are available, namely deodorants and antiperspirants [2]. Deodorants only control odor, while antiperspirants are formulated to reduce local perspiration and usually also contain components to combat bad odor. Different to deodorants, antiperspirants reduce the amount of sweat produced locally by the human body and are therefore considered drugs, since they alter the normal physiology of the body [1].

Aluminum and its derivates have a broad range of applications in many different fields, including in the cosmetics and pharmaceutical industries [4]. Many of the antiperspirant products currently used contain aluminum compounds as the active agents [5–7].

Aluminum hydrochloride (AHC) is the main active compound in antiperspirants. Its mechanism of action consists of the precipitation of AHC in the interior of the sweat glands, producing insoluble aluminum hydroxide that binds in the gland and blocks sweat secretion [1, 8]. Some antiperspirants, especially metal salt solutions, also exhibit bactericidal action and deodorant effects [7]. The skin is the main route for entry of aluminum contained in antiperspirant products, and this transdermal absorption can lead to aluminum overload, which may result in anemia, bone disease, or even dementia, notably in individuals with poor renal function [9]. The metal is potentially neurotoxic [10], so its accumulation can cause diseases such as Parkinson's, Alzheimer's, encephalopathy, and osteomalacia [11, 12]. Furthermore, the daily use of antiperspirants can irritate the skin, causing rashes and burning sensations, while more severe skin irritation can lead to desquamation or even necrosis [13].

In order to regulate the sale and use of this type of product, it is fundamental to ensure adequate supervision by governmental agencies. In Brazil, the entity responsible is the National Health Surveillance Agency (ANVISA), which stipulates a maximum of 25% of aluminum salts in the composition of antiperspirants and deodorants [14]. In Brazil, these products are classified as risk grade 2, with potential danger to health [15–17].

There are several methods that can be used to determine aluminum in antiperspirant samples, including pre-column derivatization and HPLC-UV/Vis detection [18], flow injection analysis with spectrophotometric detection [19], and atomic absorption spectroscopy [20], among others. Most of these methods require the use of organic solvents or

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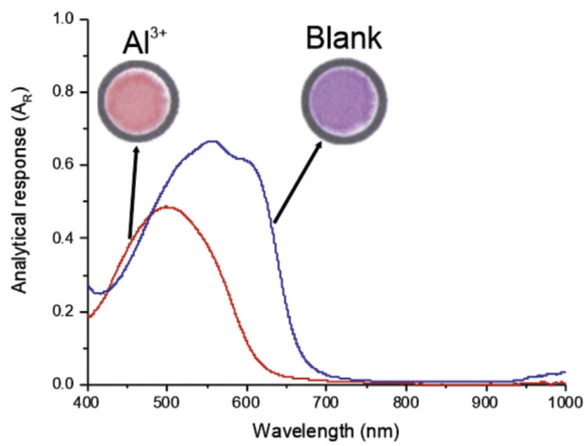

Fig. 1. Diffuse reflectance spectra of Alizarin S in alkaline medium (blue line) and the Al-Alizarin S complex (red line). Examples of spot tests for the blank and an aluminum solution.

derivatization steps, which may cause harm to the operator and the environment. Additional considerations are that the analyses can be very expensive and require specialized operators.

An alternative to these methods is to use a spot test together with diffuse reflectance spectroscopy, which is a simpler, faster, and less expensive way to determine an analyte. In this type of analysis, aliquots of the reagent and sample are placed on a solid support, with quantification by measurement of a change in the analyte, such as a color alteration or even gas evolution [21]. Paper provides a good solid platform for diffuse reflectance measurements, due its high contrast and bright white background [22]. Paper platforms can be obtained from renewable sources and require the use of minimal volumes of reagent and sample, generating a negligible waste that is easily incinerated [23]. In order to improve the analytical response and color uniformity, the paper platforms used for spot tests can be impregnated with wax, creating hydrophobic barriers so that the solutions applied are restricted to the delimited area [24]. Several studies have described low cost and portable methodologies that use hydrophobic barriers in paper [25–27].

The present work describes a method for the determination of aluminum in antiperspirant samples, using a colorimetric reaction in a spot test delimited with hydrophobic barriers in a paper platform. The reddish reaction product was measured using diffuse reflectance spectroscopy. This method is fast, cheap, eco-friendly, and very simple to use.

2. Materials and Methods

2.1. Materials and Solutions

All reagents used were analytical grade. Aluminum nitrate nonahydrate and Alizarin S were purchased from Vetec. Sodium hydroxide was purchased from Sigma-Aldrich. Solutions and dilutions employed deionized water (18.2 MΩ cm) obtained from a Milli-Q system (Millipore). A 0.1% (m/m) solution of Alizarin S in deionized water was employed for the aluminum determination. A stock solution of 1000 mg L^{-1} of aluminum was prepared in deionized water. Working solutions of aluminum were freshly prepared by appropriate dilution of the stock solution in 1.00 mol L^{-1} NaOH.

2.2. Sample Preparation

Seven different samples of antiperspirant were purchased locally in the city of Araraquara (São Paulo State, Brazil). A mass of 0.125 g of each sample was transferred to a beaker, followed by addition of 25 mL of 2.00 mol L^{-1} NaOH solution. The mixture was heated at ebullition for 5 min, under constant stirring. After cooling, the content was filtered using a quantitative paper. The beaker and the filter were washed with 50 mL of 1.00 mol L^{-1} NaOH solution, collecting the washings in a 100 mL volumetric flask that was completed to the meniscus with deionized water.

2.3. Preparation of the Paper Platform

Hydrophobic wax barriers (15 mm diameter, 0.75 mm thickness) were designed as described by Milani and co-workers [28], using graphical software (CorelDRAW X5). The printing was performed onto Whatman No. 1 filter paper, using a wax printer (Xerox Phaser 8560) and wax toner (Genuine Xerox Solid Ink Black), as described by Carrilho and co-workers [24]. The paper was heated for 120 s at 120 °C for formation of the hydrophobic barriers.

3. Methodology

In the spot test, a 15 μL aliquot of aluminum working solution or sample was applied to the center of the delimited area. After drying at room temperature, 15 μL of Alizarin S solution was added, followed by further drying for about 10 min. Diffuse reflectance measurements were performed using a portable spectrophotometer (USB2000, Ocean Optics) operated with OOIBase32 software (Ocean Optics).

3.1. Study of Matrix Interferences

Matrix interferences were evaluated using recovery tests. The sample matrix was fortified with standard solutions at levels from 50% to 200%, followed by diffuse reflectance spectroscopy measurements.

4. Results and Discussion

4.1. Preliminary Tests

The Alizarin S chromogenic reagent was selected for the colorimetric determination of aluminum in antiperspirant. In an alkaline medium, the reagent has a purple color, while reaction with Al^{3+} (Fig. 1) results in the formation of a red complex (Fig. 2) [29–31]. A strongly alkaline

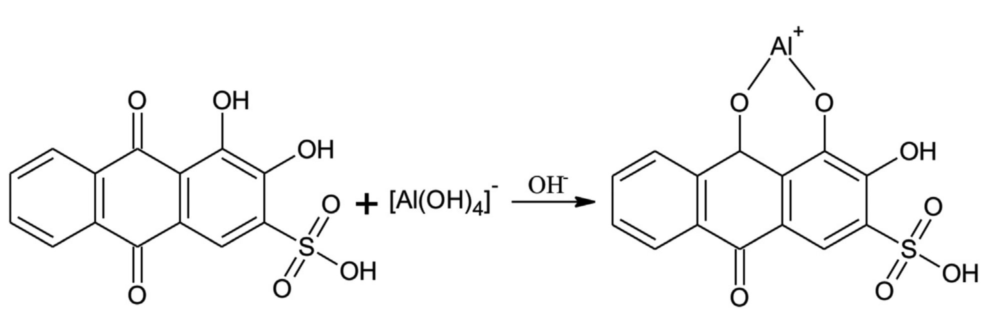

Fig. 2. Reaction between Alizarin S and aluminum in alkaline medium.

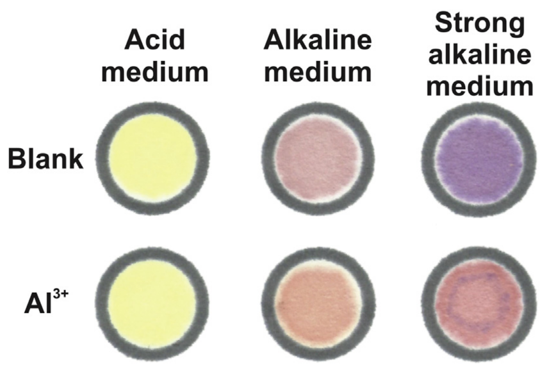

Fig. 3. Influence of pH on the reaction between aluminum and Alizarin S, and on the development of color.

medium (NaOH at 1 mol L^{-1}) was selected for use in the development of the method, due to the color difference in the presence and in the absence of aluminum (Fig. 3), which enabled the quantification of aluminum by diffuse reflectance spectroscopy. In an acid medium (pH 4), there was no development of a different color in the presence of AHC. In a neutral medium, a gelatinous precipitate of $Al(OH)_3$ was formed, while in an alkaline medium (pH 9), there was a modest color difference in the presence of aluminum, compared to the blank. Furthermore, the samples were prepared in 1 mol L^{-1} NaOH medium, eliminating a pH adjustment step for AHC determination, and due to the error in pH measurements under alkaline conditions, with a decrease in the pH value in the presence of high concentrations of Na^+, it is preferable to work with OH^- concentrations, rather than the pH scale.

Absorption by the reagent and the analyte occurs in the same wavelength range, but the reagent absorption presents a bathochromic shift. Therefore, the quantification of aluminum was achieved by measurement at 615 nm of the consumption of the purple reagent, avoiding spectral interference between the product and the reagent.

The best analytical response was achieved by first adding the aliquot of the sample or aluminum standard solution, followed by addition of the reagent solution. The use of the hydrophobic barriers provided a more homogeneous and intense coloration, decreasing the standard deviation and improving the analytical performance. The colored product was stable for at least 70 min after the reaction.

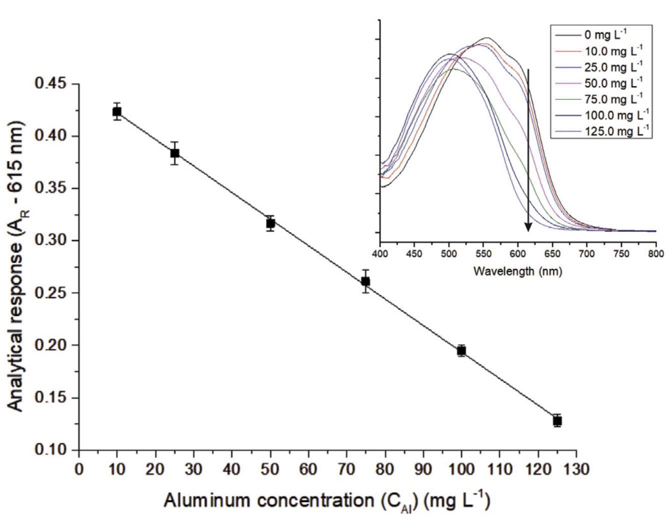

Fig. 4. Analytical curve for analytical response (A_R) vs. aluminum concentration, and the change of the absorption spectra with increase of the aluminum concentration.

Table 1
Figures of merit of the proposed method.

Parameter	Value
Linear range	10.0–125.0 mg L^{-1}
Wavelength	615 nm
Calibration curve	$A_R = 0.4479 - 0.002543\ C_{Al}$
Coefficient of correlation (R)	0.999
LOD	3.06 mg L^{-1}
LOQ	10.2 mg L^{-1}

4.2. Figures of Merit

An analytical curve was constructed using the aluminum working standard solutions at concentrations from 10 to 125 mg L^{-1}. A linear relationship was found between the analytical response (A_R, at 615 nm) and the aluminum concentration (C_{Al}), described by $A_R = 0.4479 - 0.002543\ C_{Al}$ (Fig. 4), with R = 0.999 indicating good linear correlation.

The repeatability of the proposed method was evaluated using intraday and inter-day relative standard deviations (%RSD), at two concentrations. For a 25 mg L^{-1} aluminum solution, the %RSD values were 2.7% (intra-day) and 3.0% (inter-day). The corresponding values for a 50 mg L^{-1} solution were 1.3% and 1.9%, respectively. These results showed that the new method was repeatable and could be used for the determination of aluminum in antiperspirant samples.

The limits of detection (LOD) and quantification (LOQ) were calculated according to the IUPAC recommendations [32], using the following expressions: $LOD = 3 * \sigma / S$ 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 range. The values obtained were 3.06 mg L^{-1} (LOD) and 10.2 mg L^{-1} (LOQ). The technique was sufficiently sensitive to be able to determine aluminum in antiperspirant samples. Table 1 presents the figures of merits of the proposed method.

4.3. Sample Analysis

The method developed was used to determine the concentrations of AHC in seven different antiperspirant samples (Table 2). In addition to the quantitative analysis, a semi-quantitative visual determination could be performed by comparison of the colors obtained with a color palette (Fig. 5), which would be useful in situations where no diffuse reflectance spectrometer is available.

All the samples analyzed presented aluminum hydrochloride concentrations below the limit established by legislation [14], indicating compliance of the cosmetics industries with product quality criteria intended to protect the population, with no cases of excessive quantities of aluminum that might lead to health problems in consumers.

4.4. Study of Matrix Interferences

Antiperspirants contain various other substances besides aluminum hydrochloride, such as alcohols, EDTA, glycerin, paraffin, oil, and perfume. The presence of these substances could lead to increases or

Table 2
Quantification of AHC in commercial samples using the proposed method.

Sample	AHC concentration[a] (%)
A	23.0 ± 1.8
B	19.9 ± 0.9
C	15.6 ± 0.3
D	20.2 ± 0.6
E	20.2 ± 0.6
F	11.1 ± 0.5
G	12.2 ± 0.3

[a] The maximum level allowed by Brazilian legislation is 25%.

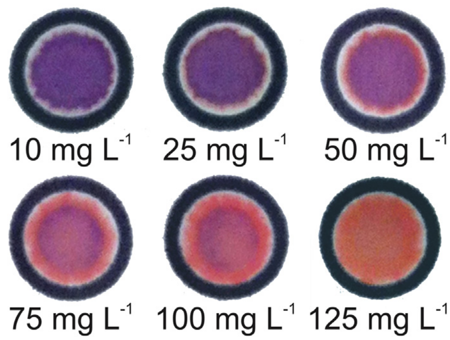

Fig. 5. Color palette for semi-quantitative visual determination of aluminum.

decreases of the analyte response, due to matrix effects. The possible existence of such effects was evaluated using recovery tests. The recovery values obtained for AHC were between 92.2% and 103.4%, indicating an absence of interference from the compounds normally found in antiperspirants. Therefore, the sample matrix had no significant influence on the AHC determination [33]. Furthermore, aluminum is the only metal present at high concentrations in these types of formulations. Consequently, if the matrix happened to be contaminated with other metals that could bind to Alizarin S, the aluminum concentration would be much higher, hence minimizing any possible interference.

5. Conclusions

A new method was developed for the determination of aluminum hydrochloride in antiperspirant samples. The methodology was successfully validated and applied in the analysis of commercial samples. The paper platform employed is environmentally friendly, because it requires minimal volumes of reagent and sample, in contrast to spectrophotometric methods. No organic solvent is used, unlike chromatographic analytical techniques, and sample clean-up is fast and simple. The paper platform is from a renewable source and is readily available, inexpensive, and can be safely disposed of by incineration. In summary, the method is simple, portable, fast, low-cost, eco-friendly, and precise.

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