Direct analysis of deodorants for determination of metals by inductively coupled plasma optical emission spectrometry

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ABSTRACT

A fast and simple dilute-and-shoot procedure for determination of Al, As, Ba, Cd, Cu, Fe, Mg, Mn, Ni, Pb, Sc, Ti, V, Zn and Zr in deodorants by inductively coupled plasma optical emission spectrometry (ICP OES) was developed. Sample preparation was carried out by diluting 1 mL of deodorant sample in 1% (v v^{-1}) HNO$_3$. The accuracy of the analytical procedure was evaluated using addition and recovery experiments, and recoveries ranged from 80 to 119%. The limits of detection varied from 0.001 to 0.76 mg kg^{-1}. Nine deodorants samples of different brands were analyzed. The maximum concentrations found (mg kg^{-1}) were: Fe (1.0), Mn (0.1), Ti (1.02), V (0.33), Zn (255.2) and Zr (0.5); for Al and Mg, determined concentrations varied from 0.01 to 7.0% and from 0.005 to 1.44 mg kg^{-1}, respectively, showing wide variation depending on the sample type. The developed procedure was adequate for determining these analytes in routine analysis presenting high sample throughput and demonstrated the feasibility of direct analysis measurements after simple dilution step.

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1. Introduction

Cosmetics, nowadays, are considered indispensable in the daily lives of people. These products besides ensuring basic care hygiene also beautify the skin of their consumers [1]. Deodorants and antiperspirants are among these largely consumed products. They have the purpose of reducing or controlling the odor of the armpits and they are presented in diverse scents, types, packages and different functions, attending the needs of several publics. Deodorants act for the purpose of preventing microbial growth or masks the substances found in sweat that cause odor. Antiperspirants, in turn, act limiting the amount of secretion of sweat glands in the region in which they were applied and reducing the sweat consequences [2,3].

The armpit cosmetics have in their composition: aluminum compounds, metal salts, alcohol, glycol, fragrances, among other components. Regarding to the safety of cosmetics, the concentrations of components in their formulation and the presence of metals may affect human health [4]. These products can trigger irritations, inflammations, and contact dermatitis [5]. Toxic metals, when absorbed in the human body, affect specific biochemical processes and they may limit the normal functions of certain enzymes [6]. Arsenic, Cd, Ni, and Pb are chemical elements prohibited in cosmetics in most developed countries (The USA, Europe, Canada, etc.) [7,8]. These elements, in turn, can accumulate in the body for a long time, being responsible for health problems, ranging from headaches, nausea, contact dermatitis, to cancer, neurological problems, cardiovascular, among others [9,10].

According to the Agência Nacional de Vigilância Sanitária (ANVISA, N° 79/2000: law 6360/1976), the maximum level of impurities allowed for artificial organic dyes in cosmetics is: 3 mg kg^{-1} for As (as As$_2$O$_3$), 20 mg kg^{-1} for Pb and 100 mg kg^{-1} for others metals [11]. The Canadian legislation establishes concentration limits for toxic elements in cosmetics, such as 5 mg kg^{-1} for As and Cd and 20 mg kg^{-1} for Pb. In addition to these metals, the legislation also establishes concentrations limits for Hg and Sb, assuming that all other metals do not present risks with respect to their toxicity

[7]. According to European Commission Regulation 1223/2009, elements as As, Ag, Cd, Cr, Hg, Mg, Ni, Se, Sr, Pb and Zr may present themselves as ingredients in cosmetics composition, as well as their salts and compounds. This regulation does not set maximum limits for concentration of impurities in these products but warns manufacturers of the responsibility to limit the contamination of trace elements at levels which do not compromise the safety of the product and consequently human health [8].

The first stage of a chemical analysis, the sample preparation step, consists of subjecting it to a suitable treatment. Thus, the procedure for decomposing a sample for analysis depends on its nature, the analyte to be determined, as well as its concentration, the method of analysis and, finally, the precision and accuracy desired [12,13]. The most conventional analytical methods used to prepare cosmetics products samples prior to the determination of metals predominantly involve the digestion of the sample with oxidant acids and heating (either in digester blocks or assisted by microwave radiation) [14–16]. However, most of these procedures, although efficient for sample decomposition may require complex laboratory equipment, high reagents consumption and increase the risk of contamination and analyte losses by volatilization [17]. In this context, simple alternatives to avoid these potential problems include direct analysis, which significantly reduces the time required for sample treatment, contributing to the principles of "green chemistry" and presents itself as a simple and efficient alternative compared to conventional sample preparation methods [18,19]. This procedure results in a very simple and fast method that generally does not require any heating and therefore prevents losses of volatile analytes before analysis, contributing greatly for accurate determination of trace elements [13,17].

All these advantages combined with the multielemental capability of ICP OES has aroused interest in its application for elemental analysis of cosmetic products. It is well-know that argon-based plasma spectroanalytical methods provide high sample throughput, high sensitivity, accuracy, robustness and low detection limits, typically in $\mu g\,L^{-1}$ range for ICP OES [20]. As ICP OES analysis usually involves the introduction of solutions in argon plasma, several procedures have been developed for pretreatment of the samples, such as: dilution using solvents, acid digestion, emulsion or micro emulsion strategies, as well direct analysis of liquid samples [21].

In this context, this work aimed the development of a simple and fast procedure, for sample treatment, using dilute-and-shoot strategy for determination of Al, As, Ba, Cd, Cu, Fe, Mg, Mn, Ni, Pb, Sc, Ti, V, Zn and Zr in deodorants by ICP OES.

2. Experimental

2.1. Samples, reagents and standards

Nine deodorant samples (DS) of different brands were selected and coded as DS1: non-perfumed; DS2: natural fresh; DS3: fresh active for men; DS4 and DS8: antibacterial action; DS5: lavender; DS6: deo-colony; DS7: fragrant and DS9: prolonged protection. The manufacturers indicate on the deodorant label that each sample contained approximately 50% $v\,v^{-1}$ ethanol solution in its composition. All analyzed samples were purchased in local pharmacies (São Carlos, SP, and Recife, PE, Brazil).

All glassware was immersed in 10% $v\,v^{-1}$ HNO_3 for at least 24 h and rinsed with ultra-pure water prior use. All aqueous solutions were prepared with analytical-grade reagents and ultrapure water, resistivity higher 18.2 MΩ cm, (Milli-Q®, Millipore, Bedford, MA, USA). Sample preparation was performed using HNO_3 (Synth, Diadema, SP, Brazil) purified in a sub-boiling distillation system (Distillacid™ BSB-939-IR,Berghof, Eningen, Germany). The analytical calibration solutions were prepared from monoelementar

Table 1
Instrumental conditions and operating parameters for ICP OES.

Instrument parameter	Operating conditions
Radio frequency applied power	1.2 kW
Sample flow rate	1.0 mL min^{-1}
Plasma gas flow rate	12 L min^{-1}
Nebulizer gas flow rate	0.50 L min^{-1}
Auxiliary gas flow rate	0.5 L min^{-1}
Replicates per sample	3
Nebulizer	V-groove
Spray chamber	Cyclonic
Analytical line (nm)	Al 394.4[a];As 189.0[a]; Ba 493.4[b]; Cd 214.4[b]; Cu 324.7[b]; Fe 239.5[b]; Mg 279.5[b]; Mn 260.5[b]; Ni 231.6[b]; Pb 220.3[b]; Sc 363.0[b];Ti 334.9[b]; V 292.4[b]; Zn 213.8[b] and Zr 339.1[a]

[a] Axial view.
[b] Radial view.

stock solutions containing 1000 mg L^{-1} of each analyte. The concentrations of standard calibration solutions ranged from 0.1 to 25 mg L^{-1}. All solutions were prepared with 1 mL of ethanol (50% $v\,v^{-1}$) and diluted up to 10.0 mL with HNO_3 0.14 mol L^{-1}, resulting in a final concentration of 5% $v\,v^{-1}$ ethanol for matrix matching. This is important for controlling transport effects during nebulization of standard solutions and samples. Argon (99.999% of purity) used for ICP OES measurements was provided by White Martins (Sertãozinho, SP, Brazil).

2.2. Instrumentation

All measurements of masses were performed using an analytical balance (Bel Engineering series M, Monza, Italy) with an accuracy of 0.001 g.

Analytical measurements were carried out using an inductively coupled plasma optical emission spectrometer with axial and radial views (iCAP 6000 Series Duo, Thermo Scientific; Cambridge, UK) equipped with a peristaltic pump, a concentric nebulizer, a cyclonic spray chamber and a quartz torch fitted with a quartz injector tube with 2.0 mm internal diameter. This instrument has a charge injection device (CID) detector and can operate in both radial and axial torch configurations. In this study, two display modes were used simultaneously in order to find the most sensitive lines. The adopted instrument operational conditions are summarized in Table 1.

Dynamic Light Scattering (DLS) analysis was performed using an ultrasound bath (Elmasonic E 30H) for sample homogenization and particle size distribution was determined by Nano Brook Omni apparatus (Brookhaven Instruments Corporation, New York, NY, USA) in combination with the software Dynamic Light Scattering Particles Sizing Software, version 1.2.1.0.

2.3. Sample preparation

Approximately 1 g of samples were weighted directly in 15.0-mL vials and subsequently, sample aliquots were diluted up to 10.0 mL with HNO_3 (0.14 mol L^{-1}). Further dilution was performed to ensure a maximum 2% ($m\,v^{-1}$) dissolved solids. Subsequently, an aliquot of each solution was appropriately diluted with deionized water, followed by quantification using ICP OES. All experiments were carried out in triplicate including blank solutions.

2.4. Addition and recovery experiments

The accuracy of the method was determined using spiked deodorant samples in two different concentration levels, 1.0 and