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Univariate and multivariate calibration strategies in combination with laser-induced breakdown spectroscopy (LIBS) to determine Ti on sunscreen: A different sample preparation procedure

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HIGHLIGHTS

- Sunscreen immobilization in a polymer for LIBS analysis.
- Ti determination using both univariate and multivariate calibration.
- Multiple linear regression presented the lowest standard error of cross-validation.

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ABSTRACT

Sunscreen is a cream which the intended use is to protect the human skin from ultraviolet radiation (UV) from the sun. Physical (inorganic) or chemical (organic) filters could be used to scatter the UV radiation, being TiO_2, one physical filter widely used in its formulation. To determine Ti concentrations on sunscreen, laborious and unsafe procedures must be performed involving strong acids and high temperatures in furnaces. With laser-induced breakdown spectroscopy (LIBS) the possibility of determining this element with minimal sample preparation is feasible. In this study, Ti concentration on sunscreen was determined through several calibration approaches (univariate and multivariate) with LIBS and an unusual sample preparation for sunscreen using a solution of poly(vinyl)alcohol (PVA) to immobilize the sample, converting its matrix to solid. Five samples were prepared and analyzed by inductively coupled plasma optical emission spectrometry (ICP OES) and the Ti concentration ranged from 0.45 to 1.58%. Standard errors for cross validation (SECV) and recoveries were 0.07% and 97–104% using multiple linear regression (MLR) with information from two Ti emission lines: I 498.17 nm and I 499.11 nm.

1. Introduction

Natural ultraviolet radiation (UV) have two main spectral regions: UV-A (320–400 nm) and UV-B (290–320 nm), which can cause harmful effects to human skin, such as burns and skin cancer [1–3]. Several countries issued recommendations alerting the population to not expose themselves directly to the sunlight many hours per day. On the other hand, many people inadvertently go to beach or tropical regions where the sunlight is usually strong. Tanning is one of the intended reasons where most people expose themselves to sunlight inappropriately and end up with sunburns. Population in general day-to-day is exposed to the sunlight and need to be careful with that.

Sunscreen is a cream which intended use is dedicated to scattering the UV-radiations. For this proposal, several inorganic (physical) and/or organic (chemical) UV-filters are added in sunscreen formulations to achieve different sun protection factor (SPF) [1,4]. Generally, one of the organic filters found in its formulations is oxybenzone (benzophenone-3) which belongs to the class of aromatic ketones known as benzophenones. This molecule was approved

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for use by the Food and Drug Administration (FDA, USA) in the early 1980s, and becomes one of the most widely used organic UVA filters on sunscreen formulations. Oxybenzone works absorbing mainly on 288 nm and 350 nm peaks of UV radiation [5]. Despite of being widely used, a substantial number of important issues regarding to safety of this compound have arisen due to its toxicopathological effects on coral planulae [6]. In order to circumvent this issue, several manufacturers increase the use of TiO_2 and ZnO nanoparticles on sunscreen formulation. The concentration of these two inorganic filters on the sunscreen formulation is directly correlated with sunscreen SPF [7], moreover, it must be careful assessed in this sun care products.

Regarding to TiO_2 compound, several studies in the literature reported methods to evaluate the concentration on the sunscreen products [7], such as: flame atomic absorption spectrometry (FAAS) [8], X-ray fluorescence (XRF) spectrometry [1,9], inductively coupled plasma optical emission spectrometry (ICP OES) [10,11], ICP-mass spectrometry (ICP-MS) [12,13], and laser-induced breakdown spectroscopy (LIBS) [4].

Even with the good performance of all studies mentioned, it is undeniable that the sunscreen sample preparation is the main difficulty. This usually consists on using strong oxidizing acids on closed vessels with assistance of microwave radiation or digestor block [2,13]. Another method employed consists in laborious process using crucible, furnace at 500 °C and acids to dissolve ashes [10].

The LIBS technique is ascending the last few years as far as analysis with minimal sample preparation is concerned. This technique consists on irradiating high-energy laser pulses on a small spot of a surface to vaporize, ionize, and excite atoms. After relaxation processes, emissions of these atoms at specific emission lines are recorded by spectrometers and a spectrum is recorded [14–17]. Sample preparation for LIBS analysis is still a challenge because direct solid analysis has obstacles to be overcome such as point-by-point signal fluctuations, micro-heterogeneity, and other problems [18]. Some of these challenges can be overcome with the use of chemometrics and several strategies are employed [19–21]. Despite of calibration difficulties on LIBS analysis, some studies are employing different strategies in several materials: suspension fertilizers [22], nickeliferous minerals [23], herbs [24], and sunscreen [4].

The goal of this study is to evaluate the concentration of Ti on sunscreen samples testing different univariate and multivariate calibration strategies in combination with LIBS data set. The sunscreen samples were immobilized on a polymer (poly(vinyl alcohol), PVA) solution, converting its matrix to solid.

2. Material and methods

2.1. Reagents and samples

The reagents used throughout this study were: deionized water (18.2 ΩM cm^{-1}) produced by a Milli-Q® Plus Total Water System (Millipore Corp., Bedford, MA, USA). Nitric acid (HNO_3, 14 mol L^{-1}; Synth, Diadema, SP, Brazil) was previously purified with assistance of a sub-boiling distillation Distillacid™ BSB-939-IR (Berghof, Eningen, Germany). Hydrofluoridric acid (HF; Nuclear, Diadema, SP, Brazil) and HNO_3 were combined to mineralize the sunscreen samples for further ICP OES analysis. Boric acid (H_3BO_3, 61.83 g mol^{-1}; Mallinckrodt, Paris, France) was used to remove remaining fluorides in the digested materials to avoid precipitation of CaF_2. A 10% w v^{-1} solution of PVA was used to immobilize the sunscreen into a polymer film. This solution was prepared using PVA Mw 89,000–98,000, 99 + % hydrolyzed (Aldrich Chemistry, St. Louis, MO, USA). Titanium stock solution containing 1000 mg L^{-1} (Merck, Darmstadt, Germany) was properly diluted in known concentrations to prepare aqueous calibration solutions for ICP OES determinations of Ti.

Five samples of sunscreen were used on this study. The samples (S1-S5) were acquired from 3 different widely known brands. S1 and S2 are from the same manufacturer (named as M1) with the SPF 30 and 70, respectively. S3 and S4 are from manufacturer M2 with the SPF 30 and 70, respectively. S5 presented the highest SPF (70) and was produced by manufacturer M3. Neither samples have special features (*e.g.* dry touch, facial sunscreen) and all described the presence of Ti on the label.

2.2. LIBS setup

The LIBS system used in this study was a J200 (Applied Spectra, Fremont, CA, USA). This instrument is a benchtop commercial system and is equipped with a 1064-nm Nd-YAG Q-switched laser with pulse duration of 8 ns. Its spectrometer consists on a 6-channel CCD with an average resolution of 70 pm and ranges from 186 to 1042 nm with 12,288 pixels. All operational parameters are controlled by Axiom software, developed by the manufacturer. The adjustable parameters are: delay time (0–2 µs), laser pulse energy (0–100 mJ), spot size (50–250 µm diameter), and laser repetition rate (1–10 Hz) while the fixed parameter is the gate width (1.05 ms). With these parameters, this equipment can reach irradiance and fluence from 0.255 GW cm^{-2} and 2 mJ cm^{-2} (250 µm spot size and 1 mJ energy) to 636.62 GW cm^{-2} and 5093 mJ cm^{-2} (50 µm spot size and 100 mJ energy), respectively, while the power ranges from 125 KW (1 mJ energy) to 12.5 MW (100 mJ energy). In this study the adjustable parameters were adapted from Sperança et al. [23]. The instrumental parameters were 75 mJ of laser pulse energy, and 100 µm of spot size. This combination provides a 955 mJ cm^{-2} fluence and 119.37 GW cm^{-2} irradiance. The delay time was 0.6 µs.

2.3. LIBS sample preparation

First, all samples were five-fold diluted in water and thoroughly homogenized with a vortex (IKA, VORTEX 1, Synth, Diadema, SP, Brazil). In this procedure, 1.000 g of the sample was accurately weighted in a 15-mL falcon tube with 4.000 g of deionized water. After that, 500 mg of this diluted sample were accurately weighted, immediately after vigorously shaking, in a 2-mL tube with 500 mg of 10% w v^{-1} PVA solution. This procedure was made in triplicate (n = 3) and the mixtures were poured into a handcraft device designed with simple components for this purpose. This device with the mixture were kept into an oven for 2 h, at 50 °C. Andrade et al. [22] and Sperança et al. [23] used the same sample preparation with slight differences. Andrade et al. [22] used the samples as received, without any handling before mixing process. Sperança et al. [23] prepared a slurry with powder mineral samples with water and, after vigorously shaking, a mass was weighted with PVA solution to make the films. The result of this process is a thin polymer film with the sunscreen encapsulated. The pictorial description of the entire procedure of sample preparation is depicted on Fig. 1.