Determination of fragrance content in perfume by Raman spectroscopy and multivariate calibration

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ABSTRACT

An alternative methodology is herein proposed for determination of fragrance content in perfumes and their classification according to the guidelines established by fine perfume manufacturers. The methodology is based on Raman spectroscopy associated with multivariate calibration, allowing the determination of fragrance content in a fast, nondestructive, and sustainable manner. The results were considered consistent with the conventional method, whose standard error of prediction values was lower than the 1.0%. This result indicates that the proposed technology is a feasible analytical tool for determination of the fragrance content in a hydro-alcoholic solution for use in manufacturing, quality control and regulatory agencies.

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1. Introduction

In the present day, perfumes can be considered as hedonic mixtures that are products of art, empirical knowledge, and science, which are composed of a combination of dozens of odorous substances and natural extracts diluted with alcohol. This heady blend is the daily partner of a growing number of people around the world [1].

Updated industry figures show the expansion of fine fragrance use in various regions of the world, and Brazil has gained a significant portion of this market, with the Brazilian consumer market currently representing nearly 16% of the worldwide perfumery market share. Sales in the country achieved 2.15 billion dollars in 2012 [2].

With the growing importance of this sector to the national population, new fragrances must be launched, imported and marketed under the tax rules of the country. For the marketing of perfumes, there is a competent law that classifies products according to the amount of concentrated fragrance "oil," and based on this classification there is a specific tax rate for the goods. According to these rules, fragrances at any concentration above 10% in ethanol are classified as perfumes. Fragrances at concentrations below 10% in ethanol are considered as eau de cologne [3].

It is noteworthy that such a classification is not universal, because international companies adopt a greater number of classifications, such as

Parfum, Soie de Parfum, Eau de Parfum, Eau de Toilette, Eau de Cologne, and Eau Fraîche, as showed below [1]:

Parfum: perfumed solution obtained by diluting 15 to 30% of the concentrated fragrance (mixture of synthetic and natural extracts) that remains noticeable for 4 to 8 h.

Soie de Parfum: perfumed solution obtained by diluting 15 to 18% of concentrated fragrance in ethanol 90°GL. Fragrance remains perceptible for 3 to 6 h.

Eau de Parfum: perfumed solution obtained by diluting 8 to 15% of the concentrated fragrance in ethanol 90°GL. The fragrance remains noticeable for 3 to 4 h.

Eau de Toilette: perfumed solution obtained by diluting 5 to 8% of the concentrated fragrance in ethanol 90°GL. Its odor is light, fruity, or citrus.

Eau de Cologne: perfumed solution obtained by diluting 3 to 5% of the concentrated fragrance in ethanol 90°GL. Essential oils are primarily citrus scents that produce a fresher odor.

Eau Fraîche or Eau de Sport: perfumed solution obtained by diluting 1 to 3% of the concentrated fragrance in ethanol 70 or 80°GL. The fragrance remains perceptible for 3 to 4 h.

Classical methods used for the analysis of fragrances are based on separation techniques such as gas or liquid chromatography (GC and LC, respectively) with various detectors, the most common being the mass selective detector (MSD) and flame ionization detector (FID) for quantification [4–6]. These techniques have the disadvantages of time

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consuming, destructive, and are not considered a green technology due to their solvent consumption [7].

In view of these disadvantages, techniques based on vibrational spectroscopy are increasingly used as they are considered easy to use, fast, and relatively inexpensive [8–10]. In particular the application of Raman spectroscopy, which has been used for many years, has expanded to fields such as the pharmaceutical sciences, geosciences, forensics, nanotechnology, cultural heritage, life sciences, and semiconductors after extensive instrumental and statistical development for data manipulation [11–15].

There are some articles describing the use of Raman spectroscopy for quantification of volatile compounds [10]. Usually, such studies generate significant amounts of information and a way to aid in the interpretation of this information is the use multivariate methods. Methods of pattern recognition and multivariate calibration are the most common techniques for extracting useful information from spectra [16].

In view of the developments in the field of analytical chemistry and the demand for process control and compliance, an analytical methodology has been proposed for determination of the fragrance content in perfumes, using Raman spectroscopy associated with chemometrics methods. This methodology is faster, non-destructive, low-cost and without the need of solvents.

2. Materials and methods

2.1. Samples preparation

Three sets of samples were prepared. The first set was water–alcohol solutions at concentrations of ethanol (K43665283 229, Merck, Germany), 20%, 40%, 60%, 80% and pure ethanol, in deionized water. The second set contained a standard fragrance developed for the study whose main compounds were: Iso e Super® (7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl naphthalene), galaxolide, dihydro myrcenol, methyl cedryl ketone, hedione, vanillin, bergamot oil, and lemon oil, which were supplied by Givaudan, Brazil. The fragrances were also diluted in pure ethanol and ethanol–water at concentrations 3%, 5%, 10%, 15%, 20%, and 25%, thus simulating various fragrance levels of commercial perfumes and colognes.

The third set contained 40 samples obtained from national and international fine fragrance companies. The total number of samples analyzed was 131.

2.2. GC-MS-FID measurements

An autosampler with 2 mL glass vials (Agilent Technologies, USA), containing perfumes and an internal standard, methyl decanoate (W505501, Sigma-Aldrich, USA), was used to inject 1 μL of sample into the GC (model 7890A, Agilent, USA). The GC was equipped with an Ultra 2 capillary column (50 m × 200 μm × 0.33 μm) from J&W Scientific (Agilent). It was used a split flow of 1:30; injector temperature
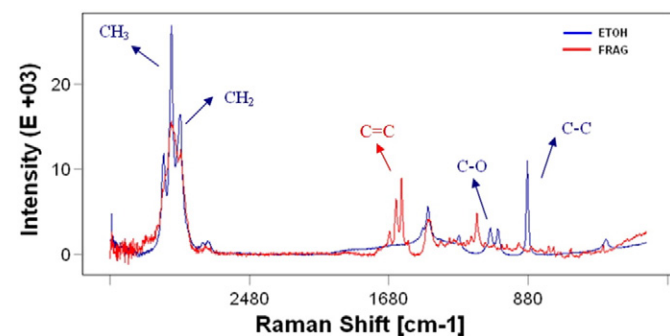

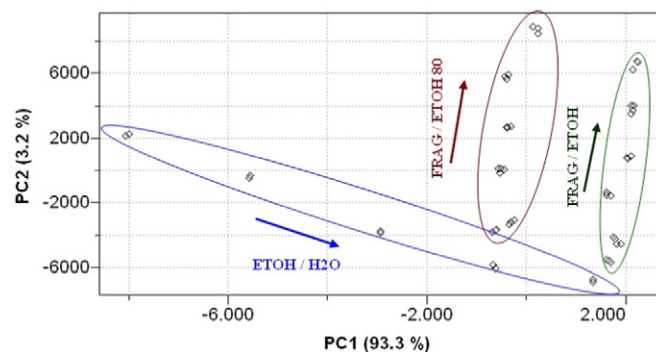**Fig. 2.** PC1 × PC2 scores for the spectra matrix data.

of 250 °C; FID temperature of 300 °C; helium as the carrier gas; ramp heating oven, 50 °C for 1 min and increased by 2 °C per minute up to 280 °C for 20 min. The MS (model 5975C, Agilent, USA) was connected to a GC with a capillary column inserted directly into the camera with an EI source (electron impact ionization), using a temperature of 230 °C for the source and 150 °C for the mass spectrometer (MS). The spectra were acquired in scan mode at an ionization energy of 70 eV.

2.3. Raman spectroscopy measurements

The Raman spectra were acquired on a RamanStation 400F spectrometer (Perkin Elmer) using a laser excitation source at 785 nm and 250 mW (in source). The device was equipped with a sample holder under automatic control, a video camera, and a two-dimensional charge-coupled device (CCD) detector cooled at −50 °C. This configuration allowed optimization of the sample position during excitation and illumination by the laser because the spectra could be monitored in real-time during acquisition, allowing the capture of intense spectra with high precision. The samples were analyzed into closed 2 mL glass vials from Agilent Technologies without any pretreatment and placed directly on the holder for analysis. All spectra were measured in the range of 200–3278 cm^{-1} using 4 scans of 3 s and a spectral resolution of 2 cm^{-1}.

2.4. Chemometric analysis

Two chemometric methods were applied in this work. Firstly, principal component analysis (PCA) was used for unsupervised pattern recognition, allowing the observation of trends and similarities between samples with different contents of water, ethanol and fragrance. After that, partial least squares (PLS) was used for multivariate calibration, in modeling the relationship between the Raman spectra and fragrance content.

Initially, a matrix (X) of experimental data should be formed containing in the columns the Raman intensities values at each
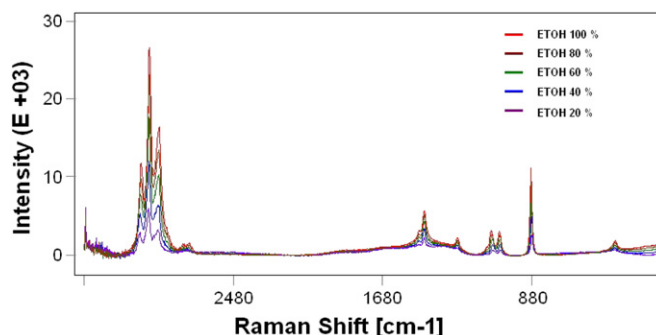

Fig. 1. Raman spectra of pure ethanol and fragrance substances with the main bands identified.

Fig. 3. Raman spectra obtained for different concentrations of ethanol and water.