10.2478/umcschem-2013-0008

ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA
VOL. LXVIII, 1-2 SECTIO AA 2013

Analysis of cosmetic products using different IR spectroscopy techniques

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This article describes the application of IR spectroscopic methods in the study of the composition of finished cosmetic products. Four spectroscopic techniques: TS (transmission spectroscopy), PAS (photoacoustic spectroscopy), ATR (attenuated total reflectance) and DRS (diffuse reflectance spectroscopy) were used for this purpose. Tested cosmetic products were of different consistency and application. The choice of spectroscopic techniques was dictated by the physical state and consistency of the sample.

1. INTRODUCTION

The cosmetic is any substance intended for external contact with the human body (skin, lips, nails, hair, teeth and mucous membranes of the mouth and external genital organs), whose aim is to keep it clean, to protect, nurture, beautify or perfume [1]. A cosmetic product put on the market can not endanger human health. In the cosmetics Act [1] there was defined the list of prohibited substances (420 substances), substances allowed in limited quantities (67 substances) and substances allowed for use in cosmetics. Among the substances permitted for the use in cosmetic formulations are dyes, preservative agents or UV protection substances. The Act also determines what information should appear on the packaging of cosmetics (trade name, manufacturer's data, ingredients, durability term, special warnings when applying, data allowing to determine the series of cosmetics). The list of cosmetic ingredients, appearing on the packaging, is written by contractual systems. INCI (*International Nomenclature of Cosmetic Ingredients*) is a naming system designed to standardize the nomenclature of ingredients.

In order to ensure the safety of their use, cosmetics are subjected to numerous tests. Research on cosmetics are divided into two groups – obligatory and additional. Clinical tests, sensory and instrumental tests belong to additional tests. Among the obligatory tests there are application tests, dermatological tests, recipe’s stability tests or the safety assessment of cosmetic products. Cosmetic product safety assessment is intended to primarily assess its composition in terms of quantity and quality [2].

In the legislation and other legal documents there have been developed a number of procedures for quantitative and qualitative analysis of finished cosmetic products and raw materials for cosmetics production. The example of such procedure may be the identification and determination of benzyl alcohol, silver nitrate or selenium disulphide in anti-dandruff shampoos. These procedures are very laborious, and their repeatability is often low, due to mistakes made during the measurements. When analyzing cosmetics and their raw materials different methods are used: chromatographic (liquid, gas and thin layer chromatography), calorimetric, acid-base titration, UV-VIS spectrophotometric, refractometric methods or mass spectrometry. These methods are associated with a specific, often laborious, sample preparation and usage of numerous measuring equipment. The analysis of the cosmetic products is difficult due to their complex composition and, as it was mentioned above, often involves variety of methods, what can increase the possibility of making mistakes and increases the time of analysis.

The solution to this problem may be the application of IR spectroscopic techniques. This is due to the fact that minimal cosmetic sample preparation is required, so that its composition is not significantly changed. The time of analysis is short and the results of such analysis are highly reproducible. Another advantage of IR spectroscopy is the ability to simultaneously obtain information about several of its components. During the analysis of cosmetic with infrared spectroscopy techniques *fingerprint* method is used, so that IR spectroscopy can be used as an analytical sifting technique. Fingerprint region (1300-700 cm^{-1}) has the characteristic arrangement of the molecules bands. This range is used to identify tested substance by comparing its spectrum with the spectrum of a model substance. The identity of both spectra in the fingerprint region is a confirmation of the identity of the tested compound with the standard one. Infrared spectroscopy methods allow not only for determination of the composition of the cosmetic product in quantitative or qualitative terms, but can also be used in assessing the effectiveness of their components [3].

Minimal sample preparation when performing measurements using IR spectroscopy techniques is very important because many times during the preparation of the sample, the composition of cosmetic products may be irreversible modified, and then the results are not reliable. However, IR spectroscopy techniques are more appropriate to determine qualitative cosmetics composition than the quantitative one. For example, the ATR technique is restricted to examine a layer of cosmetic sample what, in the case of inhomogeneity of the cosmetic formulation, does not reflect its actual quantitative composition. IR spectroscopy is a very good technique for the analysis of mineral pigments used in cosmetic products [4].

A non-destructive infrared spectroscopy has been used in the analysis of archaeological finds, including cosmetics used in prehistoric times. Using IR spectroscopy it is possible to determine the composition of cosmetics from before hundreds of years. However, it is very difficult or even impossible to determine the presence of trace amounts of the sample's components and then the application of the additional methods is advisable (chromatography, Raman spectroscopy). Usually the combination of two methods (e.g. FT-IR and Raman spectroscopy) gives more complete and more explicit knowledge about the composition of the sample [5]. Infrared spectroscopy was used to determine the presence of surfactants [6,7], emulsifiers [8] and alcohols [6].

2. MATERIALS AND METHODS

The aim of this study was to analyze the finished cosmetic products using various IR spectroscopic techniques: TS (T*ransmission Spectroscopy*), PAS (P*hotoacoustic Spectroscopy*), ATR (A*ttenuated Total Reflectance*) and DRS (D*iffuse Reflectance Spectroscopy*) and then evaluation the usefulness of those techniques in the analysis of selected cosmetics. Tested cosmetic products were of different consistency and application. The choice of spectroscopic technique was dictated by the physical state and consistency of the sample. Eye shadow, red lipstick, black eye pencil and depigmentant cream were analyzed. In the last case (depigmentant cream) photoacoustic spectroscopy could not be used because of the fact that humidity in such liquid formulation could damage the sensitive microphone in the photoacoustic cell.

TS spectra were recorded by means of Bio-Rad Excalibur FT-IR spectrometer over the 4000-600 cm^{-1} range at room temperature, resolution 4 cm^{-1} and maximum source aperture. Preparation of materials for spectroscopic measurement was based on (1) application of a small amount of the greasy sample (red lipstick, black eye pencil, depigmentant cream) on the compressed KBr pellet or, in the case of powdery materials (eye shadow), (2) the sample (~5 mg) was mixed and ground in an agate mortar with 400 mg of spectroscopically pure dry potassium bromide to a fine powder and then it was pressed to form a disk less than 1 mm thick. Data were collected in the transmission mode at room temperature under air. Interferograms of 64 scans were average for each spectrum.

FT-IR/ATR spectra were recorded at room temperature using a Nicolet 6700 spectrometer equipped with ATR detector with the diamond crystal. A sample of the tested material was mechanically pressed onto the diamond crystal. Interferograms of 64 scans were average for each spectrum.

FT-IR/DRS spectra were obtained by placing the sample mixed with a small amount of KBr in a metal container. Spectra were recorded using Nicolet 6700 spectrometer equipped with a DRS detector at room temperature, in the 4000-600cm^{-1} range. Interferograms of 256 scans were average for each spectrum. Normalization of the spectra was made by comparing the obtained spectra to the background spectrum (KBr).

FT-IR/PAS studies were performed by means of Bio-Rad spectrometer and helium purged MTEC300 photoacoustic detector, over the 4000-600 cm^{-1}. Spectra were measured at room temperature at 4 cm^{-1} resolution. The spectra were normalized by computing the ratio of a sample spectrum to the spectrum of a MTEC carbon black standard. A stainless steel cup (diameter 10 mm) was filled with a sample (thickness <6 mm). Before each data collection, the PA cell was purged with dry helium for 5 minutes. Interferograms of 1024 scans were average for each spectrum.

For a better comparison of individual bands on the IR spectra obtained for particular cosmetic products, TS, ATR, DRS and PAS spectra were normalized with respect to –CH band (2920 cm^{-1}).

3. RESULTS AND DISCUSSION

Interpretation of the IR spectra of cosmetic products is complicated due to the fact that each of the functional groups visible on the IR spectrum may be responsible for the appearance of multiple bands in a wide range of wavenumbers, so that each band may have a contribution of many functional groups. Additionally, the presence of substances such as water or paraffin compounds may are also impede the analysis. These paraffin substances are visible in the IR spectrum in the range of 3000-2800 cm^{-1} (–CH bands) and 1500-1100 cm^{-1}. Water reveals bands within 3600-2800 cm^{-1} and 1700-1300 cm^{-1} range, and those bands may overlap with the bands of tested cosmetics and hinder the interpretation of the spectra. As it was mentioned, photoacoustic spectroscopy is not an appropriate technique for the analysis of liquid cosmetics. Such samples contain in its composition a significant amount of water. The incident beam of infrared radiation could cause the evaporation of water from the sample and damage the microphone in photoacoustic detector.

For the purpose of better visibility, FT-IR spectra presented further in this work were divided into two ranges: 4000–2000 cm^{-1} (where mainly –OH and –CH groups vibrations are visible) and 2000–600 cm^{-1} (fingerprint region).

3.1. Eye shadow

Figure 1 shows the FT-IR spectra of analyzed eye shadow. In all IR spectra (PAS, TS, ATR, DRS) there are bands indicating the presence of compounds containing –CH groups: 2978, 2955, 2925, 2852, 1456, 1376 cm^{-1}. The sharp band of -OH at 3676 cm^{-1} and a broad band of SiO in the range of 1270-850 cm^{-1} indicates the presence of silica. The broad band within 3600-3000 cm^{-1} indicates the presence of intramolecular hydrogen bonding. The presence of the band with maximum at ~3070, 1560 and 670 cm^{-1} may indicate the presence of aromatic compounds in the tested cosmetic product. These bands are most apparent in the TS, PAS and DRS spectra and practically absent in the ATR spectrum. In the case of the DRS spectrum (Fig. 1b) the latter band at ~670 cm^{-1} (out-of-plane deformation vibration of aromatic rings) is slightly shifted towards higher wavenumbers (~700 cm^{-1}). This band (670 cm^{-1}) and the band at 986 cm^{-1} may also indicate the presence of talc or mica (2925, 1017 and 700 cm^{-1}) [9]. The amino group bands are visible at about 3309 and 1610 cm^{-1}, although the latter may also indicate the presence of C=O groups (ketones, esthers) [10]. The presence of ester bonds in the cosmetic can be also confirmed by the appearance of 1735 and 1715 cm^{-1} bands. These bands are absent in the ATR spectrum. Moreover, the ATR spectrum does not allow for any profound analysis. The most intense band in the ATR spectrum is the band of silica groups within 1270-900 cm^{-1} range. Although the –CH, C=O and amine groups bands have the same position in the TS, PAS and DRS spectra, large differences appear in the range of SiO groups (1270-850 cm^{-1}).

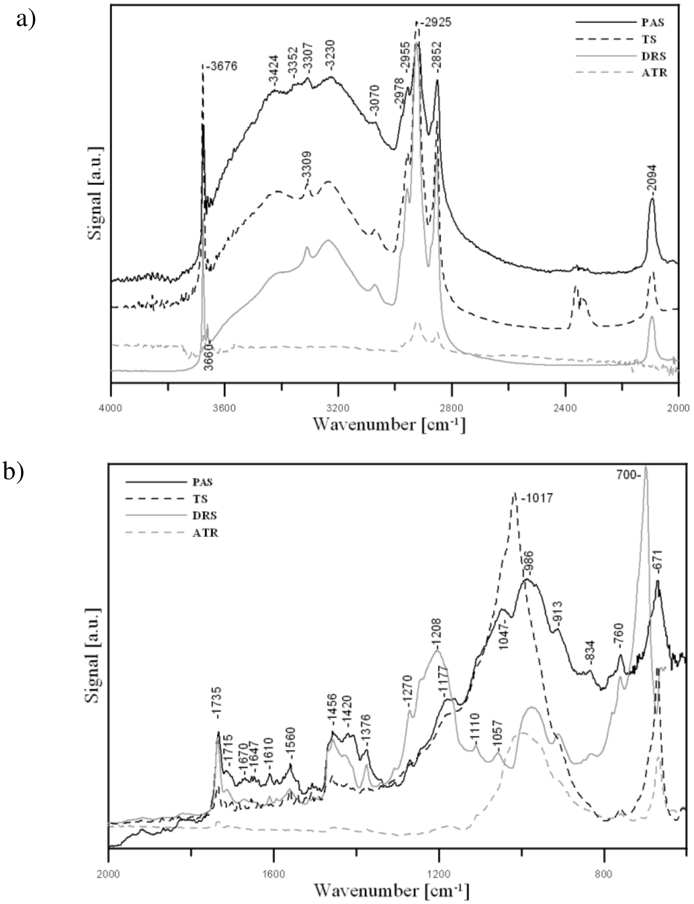

Fig. 1. FT-IR spectra of eye shadow: a) 4000-2000 cm^{-1} range, b) 2000-600 cm^{-1} range.

3.2. *Red lipstick*

Figure 2 shows the FT-IR spectra of analyzed red lipstick. In all IR spectra of tested lipstick the absorption bands have the same position, but the greatest similarity can be observed in the photoacoustic and transmission spectra. Although, there are bands in the 1650-1500 cm^{-1} range, which are not visible on ATR or DRS spectra. Additionally, the bands at 3212 and 825 cm^{-1} are present only in the photoacoustic spectrum (Fig. 2a, 2b).

Broad band in the range of 3600-3000 cm^{-1} indicates the presence of intramolecular hydrogen bonds. The bands in 3000-2800 cm^{-1} (2957, 2924, 2852 cm^{-1}) indicate the presence of aliphatic hydrocarbons in the tested cosmetic. The latter may be confirmed analyzing the spectra in the 1460-1379 cm^{-1} range (aliphatic –CH groups). The bands at ~1560 and ~1370 cm^{-1} indicate the presence of aromatic compounds. The wide band of SiO in the 1270-850 cm^{-1} range indicates the presence of silicates in considered cosmetic product. Obtained IR spectra display multiple bands which correspond to the wavenumbers characteristic for propyl ester of hexanoic acid (1743, 1460, 1418, 1379, 1363, 1163, 1109, 1040, 723 cm^{-1}) [11].

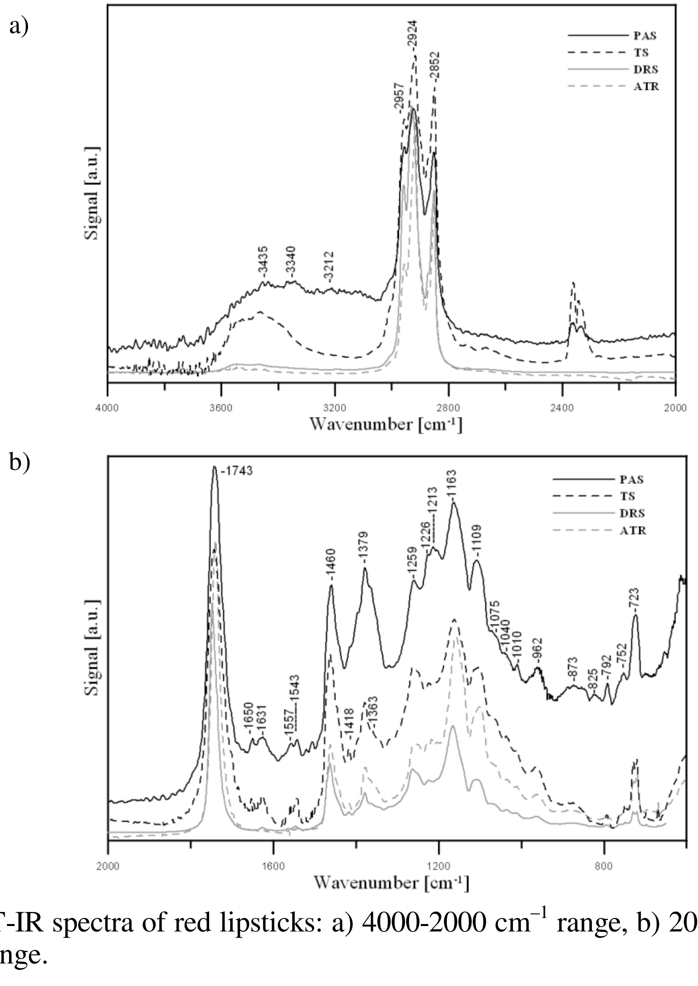

Fig. 2. FT-IR spectra of red lipsticks: a) 4000-2000 cm^{-1} range, b) 2000-600 cm^{-1} range.

3.3. Black eye pencil

While interpreting the IR spectra of black eye pencil (Fig. 3) one can observe that aromatic compounds (3026, 1750, 1450, 730 cm^{-1}), esters (1744 cm^{-1}) and amino compounds (3300, 1637 cm^{-1}) are present in the examined cosmetic. These bands are the most visible in the photoacoustic spectrum. The bands at 2953, 2921, 2851, 1456 and 1376 cm^{-1} indicate the presence of aliphatic compounds and the bands in the 1100-700 cm^{-1} range indicate the presence of silica compounds in the tested sample.

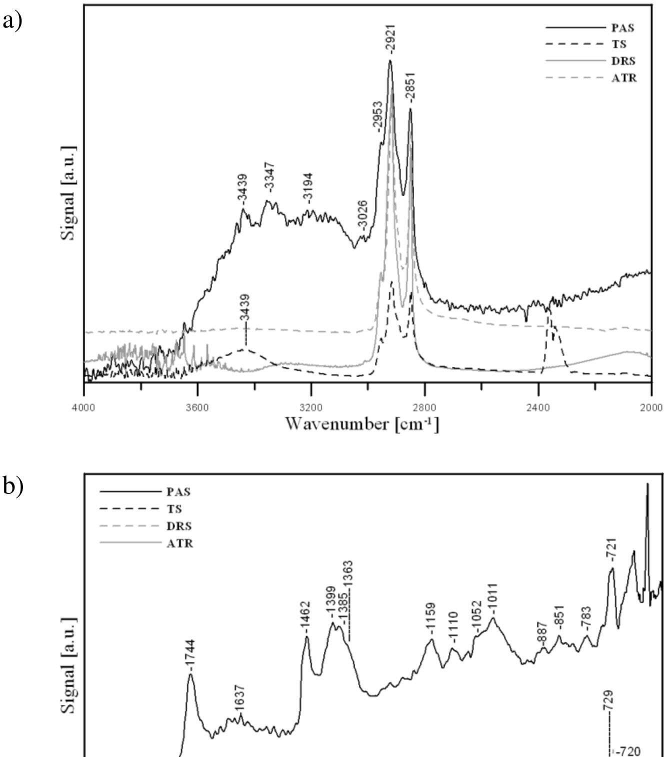

Fig. 3. FT-IR spectra of black eye pencils: a) 4000-2000 cm$^{\backslash-1}$ range, b) 2000-600 cm^{-1} range.

The bands at 2920, 2850, 1462, 1363, 1159 and 720 cm^{-1} indicate the presence of paraffin compounds. Another compound whose presence can be confirmed when analyzing the obtained IR spectra is polyethylene glycol [11]. The bands characteristic for that compound are visible at 3347, 1637, 1462, 1159, 1110 and 887 cm^{-1}. There are also bands corresponding to the presence of mica (1390, 1011 or 720 cm^{-1}) [9].

The most information about the composition of the black eye pencil can be obtained by analyzing the photoacoustic spectrum. This fact indicates that photoacoustic technique is the best IR technique for the analysis of such cosmetic product.

3.4. Depigmentant cream

Interpretation of TS and ATR spectra of depigmentant cream (Fig. 4a) and confirming the presence of water (broad and intense band in the 3700-3000 cm^{-1} range) excludes IR analysis using photoacoustic technique.

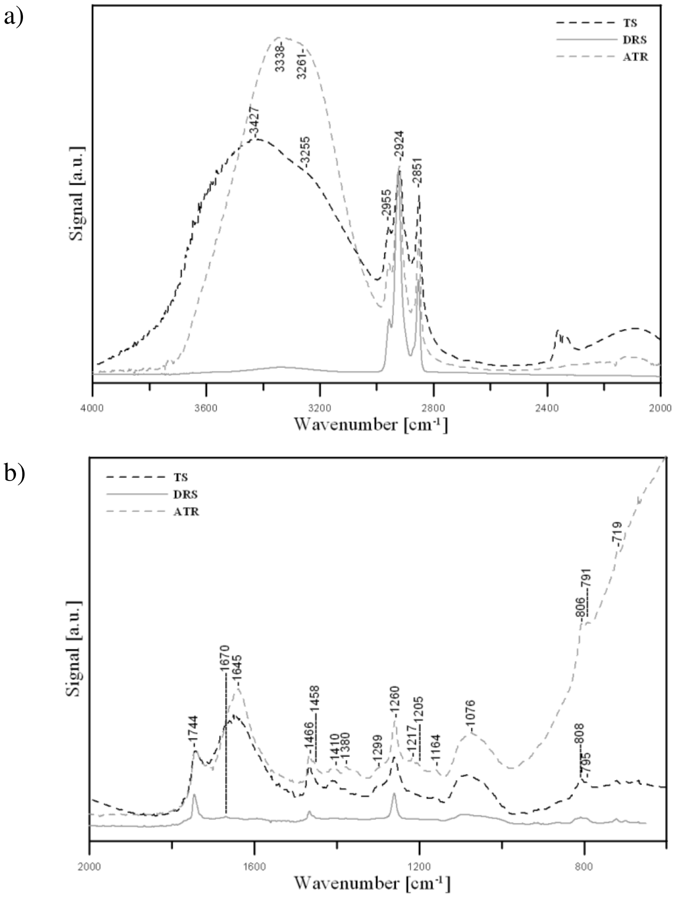

Fig. 4. FT-IR spectra of depigmentant cream: a) 4000-2000 cm^{-1} range, b) 2000-600 cm^{-1} range.

The bands appearing at ~1744 and 1645 cm^{-1} (Fig. 4b) may indicate the presence of C=O groups in carboxylic acids and aromatic ketones, respectively [10]. Another group identified on the basis of IR spectra is aliphatic –CH (2955, 2924, 2851 and 1380 cm^{-1}). The IR spectra of the tested cream have a number of bands located at wavenumbers similar to cetyl alcohol (e.g. 2955, 2851, 1466 or 719 cm^{-1}) and cyclopentasiloxane (1645, 1410, 1260, 1076 and 806 cm^{-1}) [11]. Obtained DRS spectrum is of poor quality (Fig. 4a, 4b).

4. CONCLUSION

An unambiguous analysis of the IR spectra of cosmetics is difficult due to the presence of many ingredients. The signals coming from one compound can be masked by other or may even overlap. It is hard to distinctly confirm the presence of the compound in the cosmetic, but one can confirm the presence of specific functional groups.

Based on the results presented in this paper for various types of cosmetic, the following conclusions can be made:

- similar information can be obtained by analyzing the TS and ATR spectra, the bands have similar intensity at similar wavenumbers;
- DRS spectra usually differ significantly from the TS, ATR and PAS spectra;
- DRS technique is not suitable for the analysis of liquid samples;
- in the case of liquid samples the ATR technique was the best choice, while PAS could not be used at all;
- transmission technique have to be modified in some cases (greasy samples have to be applied on the compressed KBr pellet) and the measurement had to be made relatively quickly, to avoid the destruction of KBr pellet;
- in the case of powdery samples with low water content (i.e. eye shadow) PAS and TS techniques have proved to be the best;
- the best analysis of solid samples with oil consistency (lipsticks, eyeliners) can be performed using the TS and PAS technique;

Not all techniques are suitable for the analysis of various types of cosmetics which was confirmed by research done in this work. Selection of the appropriate technique must be dictated by the physical state, the content of water, consistency and homogeneity of the cosmetic sample.

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[11] OMNIC^{TM} Specta Software, *database of spectral data*

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