

Analytical methods for identification and determination of some cosmetics ingredients

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Please cited as: CHEMIK 2011, 65, 2, 88-93

Introduction

The world's cosmetic industry is facing increasing demand for high-quality cosmetic products. Besides the usual women's interest in looking their best, recently also men have been looking for a chance to improve their facial looks. The broad range of products and the complexity of their compositions present a fearsome challenge to the analytical chemist. A look at the mixture of ingredients listed on the label of a popular face cream gives a good indication of how challenging the analysis of such a product is. Our report presents a thorough description of the analytical methodology applicable to cosmetic products. Matrices of cosmetic samples are not simple, they usually contain a high number of ingredients, and often analysis of a formulation requires extensive treatments, such as solubilisation, purification and/or preconcentration. Then the analytical signal is measured with or without previous analytical reaction. Dissolution of analytes can be carried out using either suitable chemicals and/or solvents assisted by physical complementary treatments like heating, or exposure to ultrasound or microwave radiation. In some cases strong acid or basic digestion is necessary. Sometimes, analytical procedure requires a purification/preconcentration step of the analytes of interest. To do this either solid phase or liquid-liquid extraction are employed. Distillation and headspace volatilization are seldom used. In this work analytical technique that can be applied for analysis of perfumes, aromas and UV-filters are to be discussed. Generally, methods based on previous separation step of the analytes are broadly used, with liquid chromatography (38%) being more extensively applied than gas chromatography (16%) and other techniques (Fig. 1).

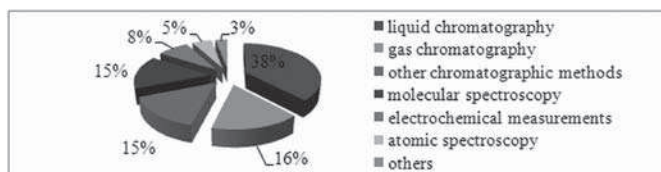


Fig. 1. Percentages of analytical techniques used for cosmetic analysis.

Perfume and aroma industry

The conventional techniques that are usually adopted to analyze a perfume/aroma are limited to: vacuum-, steam- or hydro-distillation for sample preparation, and capillary GC, capillary GC-MS or, to a lesser extent, capillary GC-FT-IR for analysis. Over the last twenty years, the perfume industry's analytical strategies used to analyze the volatile fraction that has evolved. Several factors have induced this progress, including:

- development of a new approach to headspace sampling alone or combined with other techniques, i.e. headspace solid phase micro-extraction (HS-SPME), headspace sorptive extraction (HSSE) and headspace solid phase dynamic extraction (HS-SPDE) [1]
- introduction of high-speed, inert, selective extraction techniques, such as supercritical fluid extraction (SFE), accelerated solvent extraction (ASE) and microwave-assisted extraction (MAE) [2]. The latter technique will be discussed in detail later
- dramatically increased speed of GC (Fast GC) analysis has shortened analysis times from tens of minutes to minutes or even seconds [3,4]
- introduction of comprehensive GC×GC (multidimensional gas

chromatographic technique – MDGC), which overcomes most limitations of the well-known heart-cut GC technique when separating highly complex mixtures [5,6]

- extended chiral selectivity of cyclodextrin derivatives when used as stationary phase for enantioselective GC (ES-GC), affording direct enantiomer separation of most volatile racemates [7].

Gas Chromatography and Gas Chromatography coupled with mass spectrometry

Different fragrance chemicals have been determined in cosmetic products for one reason or another. Separation techniques like chromatography are the most suitable analytical techniques for fragrances. The fragrance chemicals usually have low boiling points, and consequently gas chromatography (GC) is the technique of choice. After sample preparation and optimisation of experimental conditions, using flame ionization (FID) it is possible to determine the individual Kovats Index (KI) of each compound, which stands for a relative measurement of the retention time with respect to a group of known hydrocarbons. The identification is carried out by comparing the experimentally determined KI with the values kept in databases [8, 9]. This method can be used for identification of e.g. fragrance ingredients. Sometimes, to determine a chemical structure a mass spectrometry (MS) detector coupled with GC is used. This technique is applied to identify cosmetics ingredients, for example perfume components [9]. Figure 2 shows a mass spectrum of geraniol.

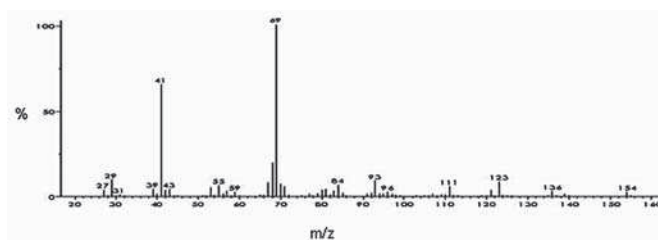


Fig. 2. Mass spectrum of geraniol

Fragrances can be classified according to their origin as they can be obtained from different sources. There are the "natural" perfumes, which are obtained from natural products, either from plants or animals, or the "synthetic" perfumes if they are based on synthetic chemicals. Essential oils, also referred to as natural perfumes are obtained from different parts of plants like flowers, fruits, roots, leaves, wood, bark, resin and seeds or from whole plants. Essential oils may also be obtained from animal glands and organs, like for example: musk which is obtained from the testicles of the musk deer, civet which is a secretion from glands of the civet cat, ambergris obtained from a secretion of the intestine of the sperm whale and finally castoreum obtained from glands near the reproductive organs of the beaver. All natural perfumes are obtained by extraction procedures described below. The appropriate process is chosen depending on the type of natural product [8].

Solvent extraction [9]

Hydrocarbon solvents, like hexane, methanol or ethanol, are added to the plant or animal material in order to extract the delicate fragrance substances. Concrete is obtained after distillation after removal of the solvent. This extract can be used as such, or cold

ethanol may be added to re-extract oils or fats in order to purify the extract. After ethanol evaporation, the oils obtained are more purified, and the extract is known as absolute. The absolute extract is the purest and most concentrated form of an essential oil. This method is helpful for fragrance chemicals which are thermolabile and/or have too high a boiling point to be extracted by the steam distillation method.

Microwave Assisted Extraction (MAE)

The microwave assisted extraction (MAE) is often chosen because microwave energy is a superior alternative to several thermal applications owing to its efficient volumetric heat production. Microwaves are electromagnetic waves in the frequency range 300 MHz to 300 GHz or of the lengths between 1 cm and 1 m. MAE is a very simple technique that permits a novel way of extracting soluble products from a wide range of materials into a fluid. Because the microwave extraction uses a combination of high temperature distribution, closed vessel and magnetic stirrer, it can give better extraction performance compared to the traditional method, i.e., distillation [10]. For example the essential rose oil is obtained by microwave assisted extraction (CEM MARS X'Press – Fig. 3) of rose buds using mixtures of acetone and hexane as solvents. Rose is an important flavour ingredient, which is a natural source of geraniol [9].

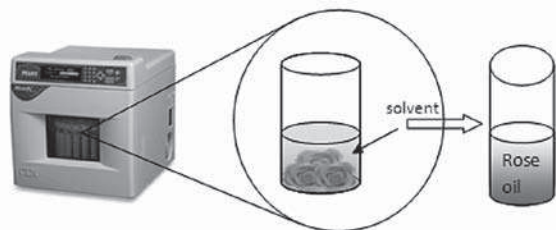


Fig. 3. Microwave assisted synthesis of rose essential oil

Solid Phase Microextraction (SPME)

SPME is a solvent-free extraction method in which analytes are directly absorbed into a fused-silica fibre coated with a polymer phase and then desorbed directly into a chromatographic injection port. This method is relatively new and was introduced by Arthur and Pawliszyn in 1990 for the analysis of pollutants in water and air environmental samples. It is very simple, quick, sensitive and versatile method of sample preparation, suitable for routine analysis of i.e. monoterpenes in tree tissues. SPME allowed all the plant material to be analyzed under the same conditions despite its wide-ranging composition, which is not always possible with other extraction methods. In this technique, an inert needle is coated with an absorbent. Depending upon the kind of coating deposited on the needle, volatiles with an affinity to the absorbent will migrate from the plant material to the needle coating and are adsorbed there [11]. This method is applied to analyze pine oil. Terpentine oil (pine oil) is used in large quantities by the fragrance industry as starting material. This oil is obtained either from balsams or from the wood of the *Pinus* genus, family *Pinaceae*. The main components of terpentine oils are terpenoid hydrocarbons. The pine oil produced in Poland contains mainly α - (~80%) and β -pinene (~5%). The former α -pinene is a fragrance substance that is used to improve the aroma of industrial products and is far more important as a starting substance in industrial syntheses of, for example, borneol, camphor, terpineols. Figure 4 shows microextraction process of pine wood, *Pinus sylvestris* [9].

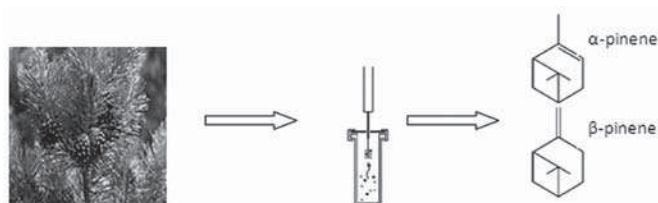


Fig. 4. Microextraction with SPME

UV filters

Although there are no official analytical methods for UV filters determination, their maximum content in sunscreen cosmetics is regulated by legislation, so analytical methods to control these products are necessary. This paper gives a review of the analytical methods for UV filters determination in cosmetics available in literature.

High performance liquid chromatography (HPLC)

The discovery of liquid chromatography is generally credited to a Russian scientist – Mikhail Tswett [12]. The meaning of the acronym “HPLC” has changed over the years. At the beginning HPLC meant High Pressure Liquid Chromatography. The combination of the column, solvent viscosity, and flow rate usually generated high pressure so HPLC can be translated as a High Pressure Liquid Chromatography. Gradually it was recognized that “high pressure” was not always present and as a consequence, “High Performance Liquid Chromatography” was substituted as a more universal term. High performance liquid chromatography HPLC is a technique ideal for analysis and purification of soluble molecules ranging from drugs to proteins. At present, HPLC is the main technique for analyses of most classes of biomolecules, including amino acids, peptides, proteins, carbohydrates, nucleic acids and lipids [13]. Nowadays analytical control of many cosmetic products is necessary for identification their compounds for example to determinate sunscreen products. Liquid chromatography is used, for quantitative determination, for UV filters named PABA, which has been banned in cosmetic products to be marketed in EU since 1992.

Chromatographic techniques especially liquid chromatography, have been, by far, the most commonly employed techniques to determine UV filters, mainly because of the fact that there are more organic UV filters than inorganic ones. Moreover it is not an easy task to determine them by direct measurement without a previous separation step because they are usually combined in cosmetic products. Although GC usually offers higher resolution than liquid chromatography (LC), the latter is usually preferred for quantitative determination of UV filters because it can deal effectively with low-volatile compounds. According to literature also GC has been employed to UV filters analysis using preliminary derivatization.

The separations are usually carried out on reversed-phase columns using modified silica columns for example C18 or C8 type. Separations carried out on normal-phase columns like silica gel (Si) are much less employed. LC coupled to MS is also used to determine UV filters. This technique was also applied to study the by-products of photo-degradation of the UV filters. Currently, HPLC combined with UV-Vis detection is the most used analytical method for determination of UV filters. The use of a diode-array detector (DAD) allows obtaining the whole UV spectrum for each peak, and it has been used for identification purposes. Solvents usually employed in chromatography include water, acetonitrile (MeCN), methanol (MeOH) and tetrahydrofuran (THF) or combinations of them, either with isocratic or with gradient elution modes. A general method that permits separation and determination of any mixture of the majority of UV filters authorized by EU legislation was proposed [14]. It allows separation of 18 UV filters with a good resolution and was validated by analysis of 27 commercial sunscreen samples. Some reagents can be added to the eluent to reduce the peak tailing of some compounds, as for example acetic acid, ethylenediaminetetraacetic acid, perchlorate and tetramethylammonium chloride, stearyltrimethylammonium chloride [e.g. 15].

The paper published by Hauri et al. [16], who was the first to employ LC coupled to MS to determine UV filters, is worth mentioning. However, MS conditions were optimised for cinnamates and camphor derivatives, and consequently salicylates are not detected and sulphonic acids give poor sensitivity.

A chronological summary of the experimental details and some remarks of the papers in which UV filters were determined in sunscreen cosmetics by LC, is given in [17].

Conclusions

Gas chromatography (GC) and mass spectrometry (MS) are by far the most important analytical techniques in the perfume industry for unravelling the composition of perfumes (i.e. perfume formulation), quality control, competitor analysis and trace analysis on substrates and in the headspace. State-of-the-art perfume formulation is based on perfume-specific Kovats Index (KI) and MS databases. Because of the complexity of perfumes, the GC columns and conditions that offer maximum resolution rather than minimum analysis time are preferably used. Recent developments in the field of comprehensive GC (i.e. GC × GC) also seem very promising for perfume analysis. The most employed analytical technique for UV filters quantitative determination is LC.

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English translation by the Author

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