

ASSESSMENT OF PERFUME INGREDIENTS WITH APHRODISIAC POTENTIAL BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Abstract

In the present study the composition of some of the best-selling perfumes of recent years has been evaluated, focusing on the quantitative assessment of potential aphrodisiac ingredients of these fragrances, such as vanillin, ethylvanillin, trans- and cis-methyl dihydrojasmonate, muskolactone and muscone. Seven samples of different brands (three women's and four men's fragrances) were analysed by gas chromatography-mass spectrometry. All the other major and minor constituents were assigned based on MS spectra library (Wiley) matching, followed by pattern analysis using chemometric data-mining (PCA). Trans-methyl dihydrojasmonate was found in all analyzed fragrances, with the highest concentration found in a perfume for women. Based on the obtained data, it seems that a common pattern of "most wanted recipe" among both men and women consumers is to be observed, based on some of the classical scents of vanilla, jasmine and musk.

Rezumat

În studiul de față, a fost evaluată compoziția unora dintre cele mai bine vândute parfumuri în ultimii ani, axându-ne pe analiza cantitativă a ingredientelor cu potențial afrodisiac cum ar fi vanilina, etilvanilina, trans-metildihidroiasomia, cis-metildihidroiasomia, muscona și muscolactona. Au fost analizate șapte parfumuri (trei pentru femei și patru pentru bărbați) prin cromatografie de gaze cuplată cu spectrometria de masă. Toți compușii au fost identificați, comparându-se spectrele de masă înregistrate cu cele din baza de date Wiley. De asemenea, s-a studiat și comparat profilul complet de ingrediente al probelor de parfum analizate prin analiză multivariată a datelor (PCA). *Trans*-metildihidroiasomia a fost găsită în toate parfumurile analizate, având cea mai mare concentrație într-un parfum pentru femei, sugerând faptul că dintre aromele clasice de vanilie, iasomie și mosc analizate, cea de iasomie este preferată atât de bărbați, cât și de femei.

Keywords: perfume, gas-chromatography, multivariate analysis, quantitative analysis

Introduction

Studies performed in the last years have been focused mainly on the analysis of perfumes in terms of potentially allergenic substances and in a lesser extent in terms of flavours that can attract consumers [1-4].

The scent marketing industry is an industry of millions of dollars and still under a continuous growth. Companies are interested in using those flavours which consumers like and make them buy the perfume [5]. Nowadays it is a huge competition among perfume producing companies and it is very difficult to find the perfect formula to attract consumers. Therefore a potential common aroma pattern in their composition is sought, which could assure the "winning" blend for men and women. Moreover, a special attention was dedicated to perfume ingredients with aphrodisiac potential, because they could play a key role in the fragrance choice and buying decision process. It is a well-known fact that aphrodisiacs may influence your

mood, increase your sexual desire and attract the opposite sex [6].

The aim of the present study was to analyse the composition of some of the best-selling perfumes of recent years, focusing on the quantitative assessment by gas chromatography-mass spectrometry of potential aphrodisiac compounds, such as vanillin, ethylvanillin, trans- and cis-methyl dihydrojasmonate, muskolactone and muscone, being frequently used as perfume ingredients for base and middle notes in perfumery such as jasmine, vanilla and musk [7, 8].

Materials and Methods

Materials, reagents and chemicals

Seven samples of the best-selling perfumes of the global market reported for the timeframe of 2010-2014 by several beauty market research companies [9-12], from different brands (three women "eau de perfume" and four men "eau de toilette") were obtained from local perfumeries and stored at room

temperature until analysis. For reasons of confidentiality, the brand names and manufacturers are not shown. They are noted as follows: no.1w, no.2w and no.3w for women fragrances and no.4m, no.5m, no.6m and no.7m for men fragrances.

Vanillin (99%), mixture of cis- and trans- methyl dihydrojasmonate ($\geq 96\%$) were obtained from Sigma Aldrich (Germany), ethyl vanillin (98%), muskolactone (98%) were obtained from Alfa Aesar (USA) and muscone from Santa Cruz Biotechnology (USA). HPLC grade methanol was used as solvent throughout the analyses. The internal standard 6-methoxy-8-nitroquinoline (99%) was purchased from Acros Organics (Belgium).

Perfume solutions

Perfumes were diluted with methanol in a ratio of 1:5, 1:50, 1:200 and stored at room temperature until analysis.

Standard solutions

Individual stock solutions of each compound were prepared in methanol at a concentration of 1 mg/mL. The internal standard solution (0.5 mg/mL) was also prepared in methanol.

GS-MS analysis

The GC-MS analysis was performed using an Agilent 7890A (GC system), Agilent 5975C inert XL EI/CI MSD with triple axis detector and an Agilent 7693 autosampler from Agilent Technologies. Separation was carried out on a Macherey-Nagel Optima 5 MS capillary column (60 m \times 250 μ m, 0.25 μ m film thickness). Helium (purity 99.999%) was employed as carrier gas at a constant column flow of 1.0 mL/min. The GC oven temperature was programmed from 60°C to 280°C at 3°C/min, and held 20 min at 280°C. Splitless mode of 1 μ L sample volume was used for injection. Electronic impact at 70 eV was used as ionization mode. The MS spectra were recorded in scan mode on the range of 50 to 800 a.m.u.

Qualitative analysis

The analytes were identified by comparison of their retention times and mass spectra with those of authentic standards. The identification was also performed by comparing the obtained mass spectra of relevant chromatographic peaks with corresponding spectra from the Wiley MS library. Multivariate data analysis was performed by using Simca v.13.0.3 (Umetrics, Sweden).

Quantitative analysis

The internal standard method was used for the quantitative analysis.

Calibration samples

From stock standard solutions, calibration solutions were prepared in methanol at individual concentrations of 0.1, 0.075, 0.05, 0.025, 0.0125, 0.005, 0.0025 and 0.0005 mg/mL of each compound. To each of them 0.25 mg/ml internal standard was added.

Perfume samples

To each analysed perfume sample 0.25 mg/mL internal standard was added.

Results and Discussion

Qualitative analysis

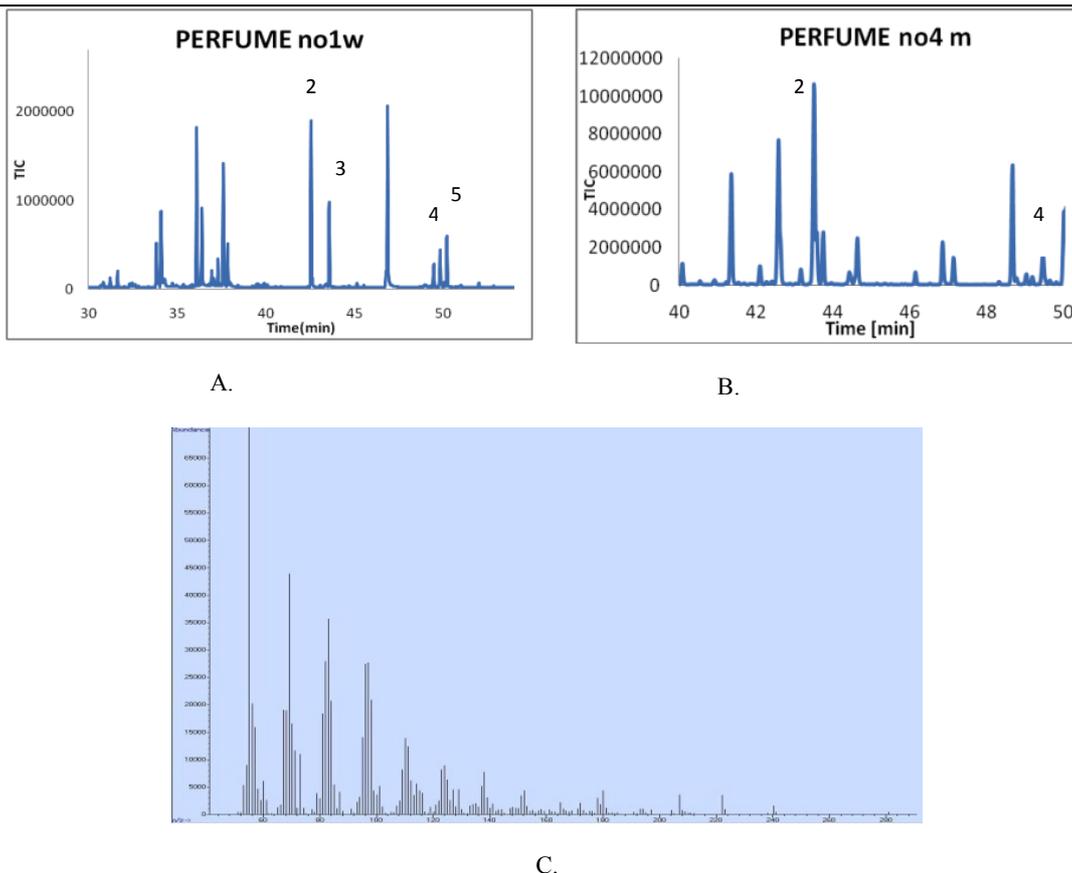
The identification of the perfume ingredients (Figure 1 A,B) was performed by comparing the obtained electron ionization mass spectra of relevant chromatographic peaks (Figure 1 C) with corresponding spectra from the Wiley MS library.

The high amount of data obtained in the perfume profiling required specific data mining tools, successfully applied in solving various basic analytical problems such as data overview, classification and/or discrimination and multivariate regression modelling [13, 14].

Therefore, multivariate data analysis based on projection methods was performed involving the entire set of compounds identified by MS library matching. Considering the nature of the available data (compounds – as variables, relative peak area fractions – as X-data) principal component analysis (PCA) was employed to identify any grouping or trends with respect of perfume composition. PCA, besides providing a first overview of the entire dataset allows extracting and displaying the systematic variation in the data matrix X. No outliers were detected in the obtained models.

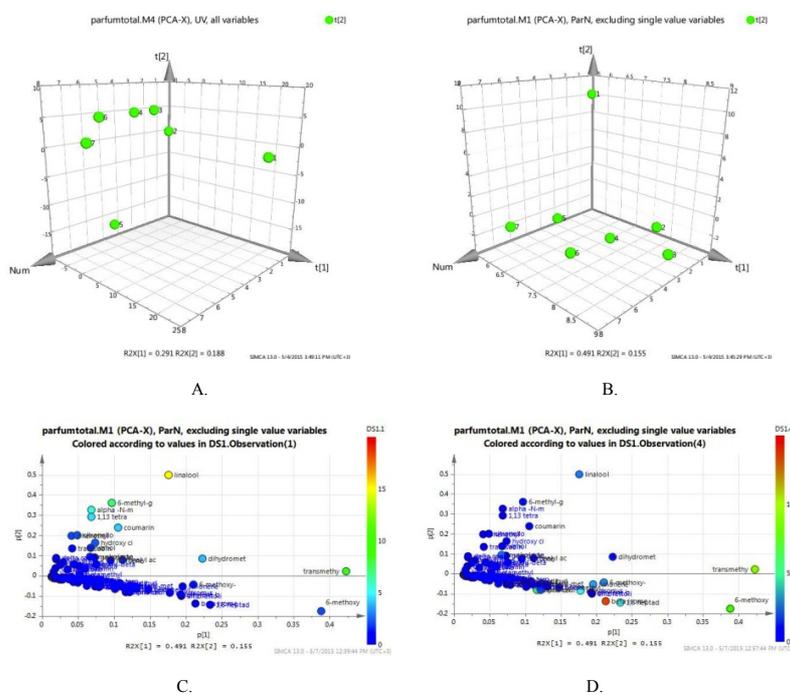
PCA performed on the available observations (N = 7, seven perfume samples) considering all the variables (K = 294) with the unit variance scaled and mean centred X-data gave a two-component model (Figure 2A), which explained 47.9% of the variation ($R^2X = 0.479$). Based on the numerous unique components identified in each of the analysed perfumes, this PCA-X model distinguishes a certain grouping of the samples (2w, 3w, 4w, 6m and 7m), whereas samples 1w and 5m seem to possess a more distinctive ingredient pattern.

Loading scatter plot of PCA-X model without single value variables, coloured according to relative peak area fractions of ingredients of sample 1w (C.), coloured according to relative peak area fractions of ingredients of sample 4m (D.).



C.
Figure 1.

Gas chromatograms of perfume samples: no.1w (A.), no.4m (B.), quantified components - (1) vanillin, (2) trans-methyl-dihydrojasmonate, (3) cis-methyl-dihydrojasmonate, (4) muskolactone, (5) muscone. Electron ionization mass spectra of muskolactone (C.)



C.
Figure 2.

Score scatter 3D plots using principal component analysis considering all variables (scaling base weight: centring and scaled to unit variance) (A.), excluding single value variables (scaling base weight: no centring, scaled to pareto variance)

As expected, by excluding the single value variables (the unique components of the analysed samples) the resulting PCA-X two-component model ($K = 81$, with scaling base weight - no centring, scaled to pareto variance) accounted for almost 65% of the variation in the X-matrix ($R^2X = 0.646$). In this case a tighter sample grouping was observed (except sample 1w), indicating certain similarities based on the shared fragrance ingredients and their relative ratio (Figure 2 B). The first component, accounting for almost 50%, captures the overall variation within the entire dataset. The loadings scatter plot (Figure 2 C and D), expressing the dominating correlation structure of the X-matrix, indicates how the X-variables vary in relation to each other, which one provide similar information, but also which ones are not well explained by the model. As it can be seen, the variables bearing the highest loadings in component one are trans- methyl dihydrojasmonate and 6-methoxy 8-nitroquinoline (internal standard), whereas linalool holds the highest loading in component two. The sample 1w seems to be somewhat different in composition compared to the other samples, and by comparing the loadings plot coloured according to the relative peak area fractions of ingredients for sample 1w (Figure 2 C) and 4m (Figure 2 D) the variables responsible for this distinction may be pointed out. Therefore, some of the compounds bearing higher loadings (e.g. linalool, dihydromethyljasmonate, 6-methyl γ -ionone) significantly differ in relative content for

sample 1w in comparison with the other analysed perfumes.

Even if at a first organoleptic evaluation of perfumes considerable differences may be noted, the performed multivariate analysis indicates that the analysed perfume samples, based on a qualitative and quantitative level, tend to share a common pattern of ingredients (except samples 1w and 5m), whereas considering the relative content of the common ingredients through the exclusion of the unique fragrance constituents ($X = 213$), only sample 1w continues to differ somewhat from the other perfumes. Therefore, even though perfumes of completely different origin were considered, in principle they tend to own considerable similitudes in terms of the nature and relative percent of constituents. Of course, more relevant conclusions may be drawn by performing similar data mining on a more extensive set of observations (perfume samples).

Quantitative analysis

Seven samples of different brands (three women's and four men's fragrance) were analysed by gas chromatography-mass spectrometry using internal standard calibration.

The chromatographic conditions were optimized to achieve the most efficient separation of the samples, with a special attention for the six reference compounds.

The content of vanillin, ethylvanillin, trans- and cis-methyl dihydrojasmonate, muskolactone and muscone in the analysed samples are shown in Table I.

Table I

Quantitative evaluation of selected perfume ingredients

Regression parameters	Vanillin	Ethyl vanillin	trans Methyl dihydrojasmonate	cis Methyl dihydrojasmonate	Muskolactone	Muscone
Slope (\pm SD)	5.07 (\pm 0.110)	6.40 (\pm 0.0821)	17.4 (\pm 0.648)	18.7 (\pm 0.724)	13.9 (\pm 0.509)	16.3 (\pm 0.601)
Intercept (\pm SD)	0.031 (\pm 0.0053)	0.018 (\pm 0.0067)	0.0010 (\pm 0.020)	0.0040 (\pm 0.0032)	0.022 (\pm 0.017)	0.028 (\pm 0.019)
R ²	0.998	0.927	0.990	0.981	0.993	0.993
Perfume sample	Content [mg/mL]	Content [mg/mL]	Content [mg/mL]	Content [mg/mL]	Content [mg/mL]	Content [mg/mL]
1w*	0.79		1.54	0.78	0.41	0.09
2w	6.57					
3w		16.09	14.71			
4m**			5.85		1.52	
5m			7.76			
6m			5.45			
7m	0.94		3.28			0.78

*w- women's perfume; **m- men's perfume

Perfume no.3w is the sweetest perfume amongst the investigated samples; most probably because it has the highest concentration of ethylvanillin responsible for the vanilla scent as a base note.

Trans-methyl dihydrojasmonate was found in the majority of analysed fragrances, based on which perfume no.3w is distinguished with a very high

concentration of this ingredient. It is also interesting to note that ingredients defining the jasmine scent are also present in men's fragrance, although being considered a feminine scent.

As expected, the sweet and animal-based fragrance of musk is to be found in highest concentrations in men's fragrances.

The small concentration of muskolactone and muscone could be explained by the fact that they are used as base notes for the musk flavour but also as fixatives increasing the effectiveness of other ingredients being called “exalting fixatives” [7, 13].

Conclusions

In the present study the composition of some of the best-selling perfumes has been evaluated, focusing on the quantitative assessment of potential aphrodisiac ingredients in these fragrances, such as vanillin, ethylvanillin, trans- and cis-methyl dihydrojasmonate, muskolactone and muscone. Trans-methyl dihydrojasmonate was found in all analysed fragrances, with the highest concentration in a perfume for women, suggesting in a way that the “winning” blend is the classic aroma of jasmine, both for men and women.

Even though perfumes of completely different origin were considered, in principle they tend to own considerable similitudes in terms of the nature and relative percent of constituents.

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