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# *Evaluation of flavour profiles in e-cigarette refill solutions using gas chromatography-tandem mass spectrometry*

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**Abstract**

Many flavour compounds that are present in e-liquids for e-cigarettes are responsible for specific tastes and smoking sensations for users. Data concerning content and specific types of flavours is often limited and unknown to users. The aim of the research was to define and compare flavour profiles of e-liquids with the same group taste from different manufacturers. Gas chromatography coupled with tandem mass spectrometry (GC-MS/MS) was used to separate and identify 90 popular compounds (98, including isomers) of interest. The developed method was validated in terms of accuracy (88-113%) for three spiking levels and the intra-day (0.2-13%) and inter-day precision (1-10%). Limits of quantitation were in the range of 10 to 816 ng/mL, while the matrix effects for 80% of the compounds were at negligible levels. The proposed method is rapid, simple and reliable and uses a green and modern GC-MS/MS technique. Twenty-five samples of five different flavours (tobacco, strawberry, cherry, menthol and apple) from five different producers were analysed, and the determined compounds were categorized and differentiated. The approach proposed in this study allowed for the evaluation of which compounds/group of compounds are responsible for taste and to distinguish common flavour compounds among the investigated brands for each flavour. Furthermore, the presented research can be considered in future toxicological studies.

**Keywords:** replacement liquids for e-cigarettes; gas chromatography-tandem mass spectrometry; flavour compounds; flavour profiles

## 1. Introduction

The availability and growing popularity of flavoured refill liquids for e-cigarettes, especially among young people, raises questions about potential adverse health implications to primary users and non-smokers exposed to second-hand smoke [1,2]. According to the Centers for Disease Control and Prevention (CDC), the use of e-cigarettes (used on at least 1 day during the past 30 days) increased dramatically from 1.5% to 11.3% among US middle and high school students during the period of 2011-2016 [3]. In turn, Filippidis *et al*. reported that the use of e-cigarettes in 27 European Union (EU) member states increased from 7.2% to 11.6% between 2011 and 2014 [4]. Notably, 81.5% of young e-cigarette users declared they use e-cigarettes "because they come in flavours I like" [5]. Manufacturers offer a wide range of flavoured refill liquids, attracting youths to e-smoking and possibly facilitating the transition to conventional smoking [6,7].

The EU Tobacco Product Directive (2014/40/EU) prohibits implementation of flavoured cigarettes; however, this regulation does not consider e-cigarettes. Moreover, there were over 7700 unique flavoured e-liquids being sold on the market according to a study conducted in 2014 [8]. In view of the above information, a chemical analysis is necessary to determine the flavour components added to e-liquids. Moreover, there is lack of studies on the effects of these additives on human cells, particularly in the lungs [9,10]. The dependence between the possible toxicity and flavour compound concentration in e-liquids is another face that requires attention [2]. Currently, there is limited data on the compounds that are responsible for specific e-liquid flavours. However, a qualitative method for the description of flavours in tobacco products has been presented [11] together with quantitative methods for the determination of the compounds in e-liquids [12–14].

The application of gas chromatography coupled to mass spectrometry (GC-MS) has aroused significant interest in the analysis of flavouring chemicals in various matrices [15–18], including e-liquids [12,14,19-21]. In the last decade, gas chromatography-tandem mass spectrometry (GC-MS/MS) has emerged as a beneficial tool in the analysis of environmental, food and forensic samples [22–24]. The use of MS/MS allows for better selectivity and sensitivity than MS-based methods, and in most cases, reduces interferences, which is crucial in multivariate flavour determination.

The aim of the present study was to evaluate the taste profiles of e-liquids and to distinguish for the first time the dependence between the e-liquid composition and a given flavour. Although, the number of flavour chemicals is large, more knowledge about the specific and known flavour profiles for a specific flavour will help to introduce additional regulation to ensure the chemicals added to e-liquids are maintained at non-toxic doses.

For this purpose, a new, highly sensitive and robust GC-MS/MS-based method was developed, which allows for the quantification of 90 (identification of 98, including isomers) flavouring chemicals in e-liquids during a single analytical run. The analytes were chosen among the compounds detected in previous studies and from commonly used flavour additives to e-liquids [11-14, 19]. To the best of the authors' knowledge, there are no scientific reports regarding the quantitation of a wide range of flavour compounds with the aid of GC-MS/MS. The applicability of the developed method was demonstrated through the analysis of 25 e-liquid samples with an expected characteristic flavour profile (menthol, apple, tobacco, strawberry and cherry) of 5 different brands.

## 2. Materials and methods

### 2.1. Reagents and standards

All standards were of analytical grade and obtained from Sigma Aldrich (St. Louis, USA): 1-amyl alcohol, 2-isopropyl-5-methyl-2-hexenal, 3,4-dihydrocoumarin, 2-acetylpyrazine, 2-acetylpyridine, 2-acetylpyrrole, 2-isopropyl-4-methylthiazole, 2-methylpyrazine, 2,5-dimethylpyrazine, 2,6-dimethylpyridine, ethyl 2-methylpropanoate, 2,3,5-trimethylpyrazine, 2,3,5,6-tetramethylpyrazine, 3-ethylpyridine, ethyl-3-methyl-3-phenylglycidate, 4-methyl acetophenone, 5-methylfurfural, anisyl acetate, benzaldehyde, α,α-dimethylphenethyl butyrate, benzyl acetate, benzyl alcohol, capric acid, carvone, citral *(*mixture of *cis and trans;* neral and geranial*)*, citronellol*, cis*-3-hexenyl acetate, *cis*-3-hexenyl-valerate, cocal, decanal, diethyl malonate, diethyl succinate, ethyl caproate, ethyl cinnamate, ethyl lactate, ethyl heptanoate, ethyl phenylacetate, ethyl vanillin, ethyl 3-(methylthio)propionate, ethyl maltol, eugenol, furaneol, furfural, furfuryl alcohol, geranyl propionate, geraniol, hedione (mixture of *cis* and *trans*), hexyl acetate, hexyl hexanoate, ionone α, ionone β, isoamyl butyrate, isoamyl isovalerate, isopentyl acetate, leaf aldehyde, leaf alcohol (*cis*-3-hexen-1-ol), limonene, linalool, linalool oxide, linalyl acetate, L-menthyl acetate, maltol, melonal, menthol, menthone, methyl cinnamate, methyl cyclopentenolone, methyl heptenone, methyl salicylate, nerol, n-hexanol, phenethyl alcohol, phenethyl isovalerate, raspberry ketone, styralyl acetate, tetrahydrolinalool, theaspirane*, trans*-2-hexenol, vanillin, β-damascone, δ-tetradecalactone, γ-valeroactone, γ-hexalactone, α-terpineol, γ-nonanolactone, γ-butyrolactone, γ-decalactone, γ-dodecalactone and δ-decalactone. Naphthalene-$d_8$ was used as the internal standard (IS) and was purchased from Isotec/Sigma-Aldrich (St. Louis, USA). Vegetable glycerine (VG) and propylene glycol (PG) were purchased from Anwit (Warsaw, Poland), and acetonitrile (ACN) (MS grade) was obtained from Merck (Darmstadt, Germany).

### 2.2. Standard solutions, calibration solutions and validation formulations

Standard stock solutions of the flavours and the IS (naphthalene-$d_8$) were prepared separately in ACN (5 mg/mL). The working standard mixture of the analytes was prepared by mixing and diluting the standard stock solutions with ACN to obtain a concentration of 25 µg/mL of each substance.

According to the labels, the main component of samples of e-liquids are: propylene glycol (above 50%), glycerine (content described as low 1-30% or in most cases as medium 30-50%) and water (content described as below 10%). The samples used for method validation were prepared as follows: 100 mg of blank laboratory made e-liquid (65% propylene glycol, 30% glycerine, 5% water, w/w/w) was spiked with an aliquot of the working standard mixture to obtain three spiking levels: 0.01, 0.08, 0.4 mg/mL, what corresponds to 100, 800 and 4000 ng/mL in the samples with a 100x dilution factor.

For furfuryl alcohol and capric acid, different spiking levels were applied: 0.03, 0.08 and 0.4 mg/mL and 0.08, 0.15 and 0.4 mg/mL, respectively. Seven calibration solutions (n=3) were prepared using a laboratory made e-liquid as the matrix in concentration ranges specific for each compound (in general, 50-5000 ng/mL). The concentration of the IS in every solution was maintained at 500 ng/mL. Validation samples were used for the evaluation of the accuracy, precision and matrix effects of the developed procedure.

### 2.3. E-liquid samples

All commercially available e-liquids samples were purchased from five companies present on the Polish market. The selection of e-liquids was based on the brand and flavour popularity. The selection of flavour was performed based on questionnaires carried out among sellers from local stores in Gdańsk about which flavours and brands are the most frequently bought by users of e-cigarettes. Five e-liquids, which were expected to have a characteristic flavour (menthol, apple, tobacco, strawberry and cherry), were purchased from each

manufacturer. For every e-liquid, the information pertaining to the presence of the primary components was provided (glycerine, propylene glycol and nicotine). In most cases, the composition (without concentration) of the flavouring compounds was included. A total of 25 e-liquid samples were selected, and the samples were analysed within two weeks of purchase after storage at room temperature in a dark place similar to the shop conditions.

### 2.4. Sample preparation

E-liquid samples were prepared prior to the analysis according to a recently published procedure [12]. Briefly, approximately 100 mg of an e-liquid sample was weighed into a 10-mL volumetric flask. Subsequently, the IS was added, and the flask filled to the mark with ACN.

### 2.5. GC-MS/MS conditions

The GC-MS/MS analyses were performed on a Shimadzu GC-2010 PLUS System (Kyoto, Japan) coupled with a Shimadzu TQ8050 triple quadrupole mass spectrometer (Kyoto, Japan). The separation of the analytes was performed on a Phenomenex ZB-5 MSi (30 m x 0.25 mm i.d., 0.25 µm film thickness) capillary column. Helium (purity ≥ 99.999%) was applied as a carrier gas at a constant flow rate of 1 mL/min. The temperature programme was set as follows: 50°C (hold for 4 min), ramp to 130°C at 10°C/min, then to 300°C (hold for 3 min) at 25°C/min. The injection volume was 1 µL in the splitless injection mode (1 min), and a solvent delay time of 2.6 min was used. The temperature of the transfer line and injector temperature was set at 285°C and 250°C, respectively. The MS was operated in electron impact (EI) mode with an electron energy of 70 eV, and the ion source temperature was set at 220°C. Argon (purity ≥ 99.999%) was applied as the collision-induced dissociation (CID) gas with a scan range that covered 30-250 m/z. For quantitation and validation, the instrument was operated in multiple reaction monitoring mode (MRM). The monitored

transitions and optimized collision energies (CEs) are listed in **Table 1**. For each compound, the characteristic transitions with the highest signal to noise ratios were selected (one quantifier, one qualifier). To verify the presence of flavour additives in each e-liquid sample, the quantifier/qualifier ion ratio relative intensity was confirmed. The following acceptance criterion for positive identification of analytes was set: relative intensities of quantifier/qualifier in the e-liquids samples should not differ by more than ±20% of those observed after analysis of standards. Chromatograms of the standards mixture and two real samples are presented in **Figure 1**. For identification, a deviation of ± 0.1 min of the expected retention time was allowed. The flavour chemicals hedione, citral, theaspirane, 2-isopropyl-5-methylhex-2-enal, epoxydihydrolinalool, α- terpineol, 3-methyl-phenylglicydate ester and menthone were detected as 2 separate single peaks due to the presence of structural isomers of these compounds.

*<insert Figure 1>*

*<insert Table 1>*

### 2.6. Flavour categorization

Compounds were divided into eight flavour categories as described in a recent study [11], namely: menthol, herbal, spicy, fruity, sweet, floral, alcoholic and miscellaneous. The main odour types for a specific flavour compound was designated from the internet database: The Good Scents Company (source: www.thegoodscentscompany.com). Each compound was assigned to one flavour category and are listed in Table 2. The assignment of particular compounds to one flavour category based on odour type is unequivocal and independent from odour threshold of specific compound. For each e-liquid, the sum of the identified compounds belonging to an adequate flavour category was calculated and expressed as a percentage of the total flavour chemical number. Additionally, the sum of the total concentration of quantified

compounds assigned to a given flavour category in the investigated e-liquids was expressed as the percentage of the total flavour concentration in each sample.

<insert Table 2>

### 2.7. Data analysis

Data processing was performed by GCMS Solution and Insight software (version 4.45, Shimadzu Corporation). Scatter plots for selected common flavour additives were constructed to separate the distribution of the analytes among the flavours and companies. To visualize the correlations of the same e-liquid flavour in terms of the identified compounds among the brands, a Venn Diagram was applied (a web tool for generating diagrams: bioinformatics.psb.ugent.be/webtools/Venn/)

## 3. 3. Results and discussion

### 3.1. Method validation

The method described in this study was validated according to the guidelines for analytical method validation [25–27].

The linearity of the calibration curves prepared in the solvent and matrix was assessed in the concentration range specific for each compound (as listed in **Table 3)** at seven concentration levels (n=3). The linearity was evaluated for each specific compound curve with coefficient of determination (r) values greater than 0.991 **(Table 3)**.

*<insert Table 3>*

The GC-MS/MS matrix effects were evaluated according to the strategy described previously [12]. Briefly, seven calibration solutions (n=3) were prepared in ACN as well as in a laboratory-made e-liquid as the matrix. The assessment of the matrix effect was performed by a comparison of the slopes of both calibration curves. The following formula was used: $ME\ [\%]=(a_m/a_s - 1)*100\%$, where $a_m$ is the slope of the calibration curve in the matrix, and $a_s$

is the slope of the calibration curve in the solvent. Approximately 80% of the compounds exhibited negligible matrix effects (≤± 20%). For the remaining compounds, medium and high matrix effects were observed (**Table 3**). The observed very high ion enhancement for some compounds (91.4%, 102.7%, 227.2% and 78% for furaneol, maltol, ethyl maltol and vanillin, respectively) is caused by the blockage of active sites in the GC inlet and column by matrix components, reducing the loss of analytes by adsorption/degradation on these active sites. The polarity and/or hydrogen binding affinity of these compounds increases their tendency to exhibit matrix-induced chromatographic enhancement. This phenomenon results in a higher analyte signal in the matrix-matched solution in comparison to the matrix-free solutions [28]. Therefore, quantification and validation were performed with the use of a matrix-matched calibration curve.

The limit of detection (LOD) was calculated according to the following formula: $LOD=3.3 * S_b/a$, where $S_b$ is the standard deviation of the intercept of the calibration curve, and $a$ is the slope of the calibration curve. The limit of quantitation (LOQ) was defined as $3*LOD$. Quantification limits varied between 10 and 816 ng/mL, which corresponded to 1 and 81.6 µg/mL in original sample, respectively, assuming a 100 time dilution of the sample.

The accuracy of the developed method was evaluated by a threefold analysis of the laboratory-made e-liquid spiked with an appropriate aliquot of analyte at three different concentration levels. The accuracy varied between 88% and 113% regardless of the spiking level. The obtained results are summarized in Table S1 in the Supplementary Material.

The data obtained during the accuracy investigation were used to assess the intra-day precision. The inter-day precision of the developed method was verified by the analysis (n=9) of the sample spiked at medium concentration level for the next three consecutive days. The precision of the method was expressed in terms of the coefficients of variation (CVs). The intra-day precision results were between 0.2 and 13%, and the inter-day precision ranged from

1 to 10%. The developed method is precise, accurate and suitable for real sample analysis. The intra- and inter-day accuracy and precision data are shown in Table S1 in the Supplementary Material.

### 3.2. Analysis of real samples

The applicability of the developed method was assessed by the analysis of 25 e-liquid samples. For each brand, five flavours (menthol, tobacco, apple, strawberry and cherry) were analysed. An overview of the components that were identified and quantified in the samples is presented in Table S2 in the Supplementary Material. The concentration of the compounds was expressed in mg/mL assuming the average density of the investigated e-liquid was equal to 1100 ± 100 mg/mL. Among the 90 investigated and determined compounds (98, including isomers), a total number of 56 flavour additives were found. Underlined compounds were indicated in the label. Manufacturers did not provide complete information regarding the content of the flavouring compounds. In some cases, compounds expected to be present in the e-liquids were not detected, while compounds not included in the label were quantified.

### 3.3. Categorization of the flavour additives

Analytes were divided into eight categories based on the odour type of each flavour found in the Good Scents Company flavour database. The categorization of the target compounds is summarized in **Table 2**. The presence of each flavour category among the investigated samples was expressed as a percentage of the total number of flavour chemicals (**Figure 2**).

*<insert Figure 2>*

The highest number of chemicals observed was for cherry-flavoured e-liquids, while the lowest, as expected, was for tobacco-flavoured liquids. Products with fruit flavours contained flavour additives categorized into multiple flavour categories, and therefore, no

252 superior flavour category emerged. An exception was made in the case of the strawberry-
253 flavoured e-liquids, which scored highest on the "fruit" category among all brands. In turn, all
254 menthol products were dominated by menthol-like components (their % contribution in the
255 total number of chemicals varied between 31% to even 75%). Surprisingly, the tobacco-
256 flavoured e-liquid group distinguished itself with the "sweet" category as the main flavour
257 category, with ethyl maltol as a most frequently occurring compound. Ethyl maltol is a widely
258 used sweet taste potentiator, despite its chemical stability in e-liquids and influence on the
259 respiratory tract is unknown [29]. E-liquids from brand C distinguish themselves with the
260 presence of menthol-like components (menthol, menthone) in the flavour composition
261 regardless of the flavour, and these components are responsible for the brand's characteristic
262 menthol flavour. The lowest number of flavour additives was observed for e-liquids from
263 brand A, while the highest was reported for brand E. Moreover, the sum of the total
264 concentration of quantified compounds assigned to a given flavour category was investigated
265 and presented as the estimated percentage of the total favour concentration in each sample
266 (**Figure 3)**.

267 *<insert Figure 3>*

268 For tobacco-flavoured products, the "sweet" category has the highest contribution in
269 total flavour chemical concentration, standing at 50% - 93%. Ethyl maltol appears to be a
270 common denominator for this category among the tobacco-flavoured e-liquids with a
271 concentration ranging from 0.013 to 0.54 mg/mL. Notably, concentration rate of menthol -
272 like components (menthol, menthone) in e-liquids with tobacco flavour from brand C is equal
273 to nearly 25%. Fruity-like components dominated the strawberry-flavoured e-liquids with a
274 percentage rate ranging from 31% to 84% and concentration ranges of 0.57 to 9.99 mg/mL.
275 The highest detected concentrations within this group have been recorded for ethyl butyrate
276 and γ-decalactone with concentration ranges equal to 0.0072 – 2.6 and 0.026 – 7.4 mg/mL,

respectively. Apple- and cherry- flavoured e-liquids contain various additives belonging to different flavour categories, therefore no dominant group among all companies in the total flavour chemical concentration can be distinguished. Surprisingly, menthol (0.62 mg/mL) was determined in one apple e-liquid (brand C) and cover 51% of total flavour concentration. For menthol products, compounds assigned with the menthol category comprised 96% - 100% of the overall determined flavour content. Additionally, no correlation has been observed between the high number of chemicals for particular flavour and their concentration.

### 3.4. 3.4 Indication of common flavour additives for a certain flavour

To identify flavour additives that are most frequently present and that may be of interest for regulatory purposes, Venn diagrams were created (**Figure 4**). By use of this tool, clear qualitative differences and similarities between the flavour composition among brands were simulated.

*<insert Figure 4>*

The Venn Diagrams show the overlap in the number of compounds identified in e-liquids of various brands within a given flavour and the presence of unique flavour additives. The diagrams show that one, two, three, two and three flavour chemicals were identified in tobacco-, strawberry-, apple-, cherry- and menthol-flavoured e-liquids, respectively, and were common for all companies; further details are includes in the description of **Figure 4**. Furthermore, flavour chemicals that were common for 80% of the e-liquids are listed. Visualization performed by the Venn diagrams allowed for the elucidation of the compounds that most frequently exist within a given flavour. Benzaldehyde, isopentyl acetate, and L-menthyl acetate have been suspected to cause irritation to respiratory passages according to Classification, Labelling and Packaging (CLP) Regulation. The indication of these specific compounds provides information as to which compounds e-cigarette users are most often exposed and may be a future concern for health researchers in view of their potential toxicity.

The amounts of the common flavour ingredients across flavours and companies are presented in the form of scatter plot (Figure 5); data are derived from Table S2 in the Supplementary Material. Ethyl maltol was detected with the highest frequency in the concentration range of 0.013 to 0.54 mg/mL (84% detection frequency), which is in agreement with previous reports [14, 30]. Vanillin (52% detection frequency) and maltol (60% detection frequency) were detected with a high frequency as well with concentration ranges equal to 0.08-2.5 mg/mL and 0.009-1.25 mg/mL, respectively. Of the analysed e-liquid samples, the highest total flavour concentration was reported for menthol-flavoured e-liquids (from 9.7 mg/mL for brand E to 17 mg/mL for brand D), while the lowest for tobacco-flavoured (from 0.024 mg/mL for brand E to 1.7 mg/mL for brand D). Menthol (identified mainly in menthol-flavoured e-liquids) was detected at the highest concentration level, equal to 12.2 mg/mL, followed by ethyl butyrate (up to 7.4 mg/ mL) and cis-3-hexenol (up to 3.2 mg/ mL). The results revealed the fluctuation of the concentration ranges among the companies. For instance, ethyl butyrate in strawberry-flavoured e-liquids was detected in the range of 0.026 to 7.4 mg/mL, benzaldehyde in cherry-flavoured – 0.043 to 1.3 mg/mL and n-hexanol in apple e-liquids in concentration ranges of 0.080 to 1.4 mg/mL. The differences in the detected concentrations of a specific flavour category are responsible for the specific taste profile of the e-liquids for a given brand. In view of the possible negative influence of some of these compounds on the respiratory tract, the evaluation of their concentration ranges in e-liquids is crucial. Additionally, an attempt was made to evaluate the correlation between the price of the e-liquid and the total amount of flavour additives (Figure S1 Supplementary Material). However, no correlation was noted. The price is dictated entirely by the manufacturer and is unrelated to the e-liquid composition.

*<insert Figure 5>*

## 4. Conclusions

In this study, a rapid and sensitive GC-MS/MS method for the quantitation of 90 flavour additives in replacement liquids for electronic cigarettes, i.e., less than 22 min, has been developed. This approach based on the categorization of flavour chemicals allowed for an evaluation of the taste profiles used in e-liquids and the distinct correlation between the e-liquid composition and given flavour. The information about specific flavour compounds (and their concentration ranges) responsible for the overall flavour of e-liquids, regardless of the manufacturer, may be beneficial in future toxicological studies. The toxicological evaluation of many flavouring compounds in e-liquids is difficult to perform. It is crucial to differentiate common compounds responsible for a certain flavour, which any e-cigarette user is exposed to, as well as the most frequently present additives. Thus, the developed method for qualitative and quantitative determination of popular flavour additives in e-liquids might be suitable in quality control laboratories. Future studies should focus on the use of human pulmonary fibroblasts to model the effects of e-liquid components on lung cells together with concentration determination. This type of research would be an integral part of improving the surveillance of e-cigarette products and categorizing hazardous compounds.

## 5. References

[1] U.S. Department of Health and Human Services. E-Cigarette Use Among Youth and Young Adults: A Report of the Surgeon General. 2016. https://e-cigarettes.surgeongeneral.gov/documents/2016_sgr_full_report_non-508.pdf (accessed 12. 11. 2017).

[2] A. Khlystov, V. Samburova, Flavoring Compounds Dominate Toxic Aldehyde Production during E-Cigarette Vaping, Environ. Sci. Technol. 50 (2016) 13080-13085

[3] W.V. No, A. Jamal, A. Gentzke, S.S. Hu, K.A. Cullen, B.J. Apelberg, D.M. Homa, B.A. King, Morbidity and Mortality Weekly Report Tobacco Use Among Middle and

High School Students — United States, 2011 – 2016, Weekly, 66 (2017) 597-603

[4] F.T. Filippidis, A.A. Laverty, V. Gerovasili, C.I. Vardavas, Two-year trends and predictors of e-cigarette use in 27 European Union member states, Tob. Control, 0 (2016) 1–7.

[5] B.K. Ambrose, B. Rostron, N. Borek, Flavored Tobacco Product Use Among US Youth Aged 12-17 Years, 2013-2014, JAMA, 314 (2015) 1871-1873.

[6] World Health Organization Study Group on Tobacco Product Regulation, Report on the scientific basis of tobacco product regulation: third report of a WHO study group,2009, http//apps.who.int/iris/bitstream/10665/44213/1/9789241209557_eng.pdf (accessed 12.11.2017)

[7] C.A. Stanton, A.C. Villanti, C. Watson, C.D. Delnevo, Flavoured tobacco products in the USA : synthesis of recent multidiscipline studies with implications for advancing tobacco regulatory science, Tob. Control, 25 (2016) ii1-ii3.

[8] S. Zhu, J.Y. Sun, E. Bonnevie, S.E. Cummins, A. Gamst, L. Yin, M. Lee, Four hundred and sixty brands of e-cigarettes and counting: implications for product regulation, Tob. Control, 23 (2014) iii3–iii9.

[9] C.A. Lerner, I.K. Sundar, H. Yao, J. Gerloff, D.J. Ossip, S. Mcintosh, R. Robinson, I. Rahman, Vapors Produced by Electronic Cigarettes and E-Juices with Flavorings Induce Toxicity, Oxidative Stress, and Inflammatory Response in Lung Epithelial Cells and in Mouse Lung, PLoS One, 10 (2015) 1–26.

[10] C. I. Vardavas, C. Girvalaki, F.T. Filippidis, M. Oder, R. Kastanje, I. de Vries, L. Scholtens, A., S. Plackova, R. Turk, L. Gruzdyte, F. Rato F, D. Genser, H. Schiel H, A. Balázs A, E. Donohoe E, A.I. Vardavas, M.N. Tzatzarakis, A.M. Tsatsakis AM, P.K. Behrakis. Characteristics and outcomes of e-cigarette exposure incidents reported to 10 European Poison Centers: a retrospective data analysis, Tob. Induc. Dis. 15 (2017) 1-7.

[11] E.J.Z. Krüsemann, W.F. Visser, J.W.J.M. Cremers, J.L.A. Pennings, Identification of flavour additives in tobacco products to develop a flavour library, Tob. Control, 0

(2017) 1–7.

[12] J. Aszyk, M. K.Woźniak, P. Kubica, A. Kot-Wasik, J. Namieśnik, A. Wasik, Comprehensive determination of flavouring additives and nicotine in e-cigarette refill solutions . Part II : Gas-chromatography – mass spectrometry analysis, J. Chrom. A 1517 (2017) 156–164.

[13] J. Aszyk, P. Kubica, A. Kot-Wasik, J. Namieśnik, A. Wasik, Comprehensive determination of flavouring additives and nicotine in e-cigarette refill solutions . Part I : Liquid chromatography-tandem mass spectrometry analysis, J. Chrom. A, 1519 (2017) 45–54.

[14] P.A. Tierney, C.D. Karpinski, J.E. Brown, W. Luo, J.F. Pankow, Flavour chemicals in electronic cigarette fluids, Tob. Control, 25 (2015) 10-15.

[15] A. Chaintreau, D. Joulain,C. Marin, C.O. Schmidt, M. Vey, GC-MS Quantitation of Fragrance Compounds Suspected To Cause Skin Reactions, J. Agric. Food Chem. 51 (2003) 6398–6403.

[16] B. Desmedt, M. Canfyn, M. Pype, S. Baudewyns, V. Hanot, P. Courselle, J.O. De Beer, V. Rogiers, K. De Paepe, E. Deconinck, HS – GC – MS method for the analysis of fragrance allergens in complex cosmetic matrices, Talanta, 131 (2015) 444–451.

[17] V. Ivanova, M. Stefova, T. Stafilov, B. Vojnoski, I. Bíró, A. Bufa, F.Kilár, Validation of a Method for Analysis of Aroma Compounds in Red Wine using Liquid – Liquid Extraction and GC – MS, Food Anal. Methods, 5 (2012) 1427–1434.

[18] P. Lopez, M. Van Sisseren, S. De Marco, A. Jekel, M. De Nijs, H.G.J. Mol, A straightforward method to determine flavouring substances in food by GC – MS, Food Chem. 174 (2015) 407–416.

[19] C. Hutzler, M. Paschke, S. Kruschinski, F. Henkler, J. Hahn, A. Luch, Chemical hazards present in liquids and vapors of electronic cigarettes, Arch. Toxicol. 88 (2014) 1295–1308.

[20] K.E. Farsalinos, K.A. Kistler, G. Gillman, Evaluation of Electronic Cigarette Liquids

406 and Aerosol for the Presence of Selected Inhalation Toxins, Nicotine Tob. Res. 17
407 (2015) 168–174.

408 [21] M.L. Feo, E. Eljarrat, D. Barceló, Performance of gas chromatography / tandem mass
409 spectrometry in the analysis of pyrethroid insecticides in environmental and food
410 samples, Rapid. Commun. Mass Spectrom. 25 (2011) 869–876.

411 [22] C. Vardavas, C. Girvalaki, A. Vardavas , S. Papadakis, M. Tzatzarakis, P. Behrakis,
412 A. Tsatsakis, Respiratory irritants in e-cigarette refill liquids across nine European
413 countries: a threat to respiratory health? Eur. Respir. J. 50 (2017) 1701698.

414 [23] C.M. Mayr, D.L. Capone, K.H. Pardon, C.A. Black, D. Pomeroy, I.L. Francis,
415 Quantitative Analysis by GC-MS/MS of 18 Aroma Compounds Related to Oxidative
416 Off -Flavor in Wines, J. Agric. Food Chem. 63 (2015) 3394-3401.

417 [24] M. K. Woźniak, M. Wiergowski, J. Aszyk, P. Kubica, J. Namieśnik, M.Biziuk,
418 Application of gas chromatography–tandem mass spectrometry for the determination
419 of amphetamine-type stimulants in blood and urine, J. Pharm Biomed. Anal. 148
420 (2017) 58-64.

421 [25] C.C. Chan, H. Lam, Y.C. Lee, X.-M. Zhang, Analytical method validation and
422 instrument performance verification, John Wiley & Sons, Hoboken, 2004, 27-66;173-
423 196.

424 [26] Guidance for Industry Q2B Validation of Analytical Procedures: Methodology.
425 https://www.fda.gov/downloads/drugs/guidances/ucm073384.pdf (accessed
426 12.11.2017).

427 [27] Commission Decision 2002/657/EC of 12 August 2002 implementing Council
428 Directive 96/23/EC concerning the performance of analytical methods and the
429 interpretation of results, OJEC L221 (2002) 8-36.

430 [28] M.M. Rahman, J. Jang, J.H. Park, A.M. Abd El-Aty, A.Y. Ko, J.H. Choi, A. Yang,
431 K.H. Park, J.H. Shim, Determination of kresoxim-methyl and its thermolabile

metabolites in pear utilizing pepper leaf matrix as a protectant using gas chromatography, J. Adv. Res. 5 (2014) 329-335.

[29] S. Miao, E.S. Beach, T.J. Sommer, J.B. Zimmerman, S. Jordt, High-Intensity Sweeteners in Alternative Tobacco Products, Nicotine Tob. Res. 18 (2016) 2169–2173.

[30] M.P. Kavvalakis, P.D. Stivaktakis, M.N. Tzatzarakis, D. Kouretas, J. Liesivuori, Multicomponent Analysis of Replacement Liquids of Electronic Cigarettes Using Chromatographic Techniques, J. Anal. Toxicol. 39 (2015) 262–269.

442 *List of tables*

443 ***Table 1.*** *Monitored ion transitions and collision energies*

| Lp. | Compound name | Molecular formula | Retention time [min] | MRM transition, m/z (quantitative) | CE [V] | MRM transition, m/z (qualitative) | CE [V] | Ion ratio |
|---|---|---|---|---|---|---|---|---|
| 1 | Ethyl 2-methylpropanoate | $C_5H_{10}O_2$ | 3.835 | 88.00>73.10 | 10 | 88.00>55.00 | 18 | 100/33 |
| 2 | 1-amylalcohol | $C_5H_{12}O$ | 3.96 | 70.00>55.10 | 6 | 55.00>53.10 | 10 | 100/64 |
| 3 | Ethyl butyrate | $C_6H_{12}O_2$ | 4.39 | 88.00>61.10 | 6 | 88.00>60.00 | 6 | 100/61 |
| 4 | Ethyl lactate | $C_5H_{10}O_3$ | 5.157 | 75.00>45.10 | 6 | - | | |
| 5 | 2-methylpyrazine | $C_5H_6N_2$ | 5.320 | 94.00>67.10 | 10 | 94.00>53.10 | 14 | 100/45 |
| 6 | Furfural | $C_5H_4O_2$ | 5.550 | 95.00>67.00 | 6 | 96.00>68.00 | 10 | 100/97 |
| 7 | Leaf aldehyde | $C_9H_{14}O$ | 5.980 | 83.00>55.10 | 6 | 83.00>53.00 | 14 | 100/6 |
| 8 | Furfuryl alcohol | $C_5H_6O_2$ | 6.003 | 98.00>70.10 | 6 | 81.00>53.10 | 10 | 100/43 |
| 9 | Cis-3-hexenol | $C_6H_{12}O$ | 6.100 | 82.00>67.10 | 6 | 67.00>65.10 | 18 | 100/20 |
| 10 | Trans-2-hexenol | $C_6H_{12}O$ | 6.323 | 82.00>67.10 | 6 | 82.00>65.10 | 18 | 100/28 |
| 11 | n-Hexanol | $C_6H_{14}O$ | 6.363 | 69.00>67.10 | 6 | 56.00>54.00 | 10 | 100/37 |
| 12 | Isopentyl acetate | $C_7H_{14}O_2$ | 6.510 | 70.00>55.10 | 10 | 70.00>53.00 | 18 | 100/64 |
| 13 | 2,6-dimethylpyridine | $C_7H_9N$ | 6.673 | 107.00>65.10 | 22 | 107.00>92.10 | 14 | 100/45 |
| 14 | 2,5-dimethylpyrazine | $C_6H_8N_2$ | 7.227 | 108.00>81.10 | 10 | 108.00>67.10 | 10 | 100/74 |
| 15 | γ-butyrolactone | $C_4H_6O_2$ | 7.300 | 86.00>42.10 | 6 | 86.00>57.90 | 6 | 100/65 |
| 16 | γ-valeroactone | $C_5H_8O_2$ | 8.123 | 85.00>57.10 | 6 | 85.00>74.00 | 26 | 100/62 |
| 17 | 3-ethylpyridine | $C_7H_9N$ | 8.207 | 92.00>65.10 | 10 | 107.00>92.10 | 14 | 100/99 |
| 18 | Benzaldehyde | $C_7H_6O$ | 8.277 | 106.00>77.10 | 18 | 77.00>51.10 | 14 | 100/85 |
| 19 | 5-methylfurfural | $C_6H_6O_2$ | 8.330 | 109.00>53.00 | 14 | 110.00>53.10 | 22 | 100/89 |
| 20 | Methyl heptenone | $C_8H_{14}O$ | 8.793 | 108.00>93.00 | 2 | 108.00>69.00 | 10 | 100/63 |
| 21 | Ethyl caproate | $C_8H1_6O_2$ | 9.027 | 88.00>61.10 | 6 | 99.00>71.10 | 6 | 100/52 |
| 22 | 2,3,5-trimethylpyrazine | $C_7H_{10}N_2$ | 9.077 | 122.00>81.10 | 10 | 122.00>54.20 | 18 | 100/22 |
| 23 | Cis-3-hexenylacetate | $C_8H1_4O_2$ | 9.177 | 82.00>67.10 | 6 | 67.00>65.10 | 10 | 100/85 |
| 24 | 4-methyl-2-(1-methylethyl)-thiazole | $C_5H_7NOS$ | 9.407 | 126.00>73.00 | 10 | 141.00>126.00 | 10 | 100/37 |
| 25 | 2-acetylpyrazine | $C_6H_6N_2O$ | 9.460 | 122.00>94.10 | 6 | 80.00>53.10 | 10 | 100/99 |
| 26 | Methyl cyclopentenolone | $C_6H_8O_2$ | 9.653 | 112.00>84.10 | 6 | 112.00>56.10 | 14 | 100/39 |
| 27 | 2-acetylpyridine | $C_7H_7NO$ | 9.687 | 79.00>52.10 | 14 | 121.00>79.00 | 14 | 100/65 |
| 28 | Limonene | $C_{10}H_{16}$ | 9.690 | 93.00>77.10 | 10 | 93.00>91.10 | 10 | 100/89 |
| 29 | Benzyl alcohol | $C_7H_8O$ | 9.750 | 79.00>77.10 | 14 | 108.00>79.10 | 14 | 100/89 |
| 30 | Melonal | $C_9H_{16}O$ | 10.067 | 82.00>67.10 | 10 | 67.00>65.10 | 10 | 100/66 |
| 31 | γ- hexalactone | $C_6H_{10}O_2$ | 10.077 | 70.00>55.10 | 6 | 85.00>57.00 | 6 | 100/15 |
| 32 | Isoamyl butyrate | $C_9H_{18}O_2$ | 10.083 | 89.00>71.10 | 6 | 71.00>56.10 | 10 | 100/98 |
| 33 | Furaneol | $C_6H_8O_3$ | 10.170 | 128.00>85.00 | 6 | 85.00>57.10 | 6 | 100/31 |
| 34 | 2-acetylpyrrole | $C_6H_7NO$ | 10.263 | 109.00>94.10 | 10 | 94.00>66.10 | 10 | 100/90 |
| 35 | Diethyl malonate | $C_7H_{12}O_4$ | 10.333 | 133.00>115.10 | 6 | 133.00>87.00 | 14 | 100/71 |
| 36 | Epoxydihydrolinalool (1. isomer) | $C_{10}H_{20}O_2$ | 10.430 | 94.00>79.10 | 10 | 94.00>77.10 | 22 | 100/55 |
| 37 | 2,3,5,6-tetramethylpyrazine | $C_8H_2N_2$ | 10.647 | 136.00>54.10 | 14 | 136.00>95.10 | 10 | 100/81 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 38 | Epoxydihydrolinalool (2. isomer) | $C_{10}H_{20}O_2$ | 10.703 | 94.00>79.10 | 10 | 94.00>77.10 | 22 | 100/48 |
| 39 | Ethyl heptanoate | $C_9H_{18}O_2$ | 10.817 | 88.00>61.00 | 6 | 88.00>70.10 | 2 | 100/55 |
| 40 | Tetrahydrolinalool | $C_{10}H_{22}O$ | 10.840 | 73.00>55.10 | 10 | 73.00>58.10 | 18 | 100/52 |
| 41 | Geranyl propionate | $C_{13}H_{22}O_2$ | 10.847 | 82.00>67.10 | 6 | 67.00>65.00 | 10 | 100/60 |
| 42 | Linalool | $C_{10}H_{18}O$ | 10.867 | 93.00>77.10 | 14 | 93.00>91.10 | 6 | 100/87 |
| 43 | Ethyl-3-methylthiopropionate | $C_6H_{12}O_2S$ | 10.873 | 148.00>74.10 | 6 | 74.00>59.00 | 14 | 100/78 |
| 44 | Isopentyl isovalerate | $C_{10}H_{20}O_2$ | 10.960 | 70.00>55.10 | 10 | 85.00>57.10 | 6 | 100/54 |
| 45 | 2-Isopropyl-5-methylhex-2-enal (1. isomer) | $C_{10}H_{18}O$ | 11.013 | 111.00>55.00 | 14 | 97.00>69.10 | 6 | 100/98 |
| 46 | 2-Isopropyl-5-methylhex-2-enal (2. isomer) | $C_{10}H_{18}O$ | 11.137 | 111.00>55.10 | 14 | 111.00>93.00 | 6 | 100/56 |
| 47 | Maltol | $C_6H_6O_3$ | 11.180 | 126.00>71.10 | 14 | 126.00>55.10 | 22 | 100/36 |
| 48 | Phenylethyl alcohol | $C_8H_{10}O$ | 11.193 | 91.00>65.10 | 14 | 122.00>92.10 | 6 | 100/29 |
| 49 | Menthone (1. isomer) | $C_{10}H_{18}O$ | 11.833 | 112.00>97.00 | 6 | 112.00>70.00 | 14 | 100/81 |
| 50 | Benzyl acetate | $C_9H_{10}O_2$ | 11.960 | 108.00>79.10 | 14 | 108.00>77.10 | 26 | 100/50 |
| 51 | Menthone (2. isomer) | $C_{10}H_{18}O$ | 12.020 | 112.00>97.30 | 10 | 112.00>70.00 | 10 | 100/72 |
| 52 | Menthol | $C_{10}H_{20}O$ | 12.123 | 81.00>79.10 | 14 | 81.00>53.10 | 14 | 100/91 |
| 53 | Diethyl succinate | $C_8H_{14}O_4$ | 12.153 | 129.00>101.10 | 6 | 101.00>73.00 | 6 | 100/62 |
| **IS** | Naphtalene-$d_8$ | $C_{10}D_8$ | 12.277 | 136.00>108.10 | 22 | 136.00>84.10 | 22 | 100/50 |
| 54 | 4'-methylacetophenone | $C_9H_{10}O$ | 12.307 | 119.00>91.10 | 10 | 91.00>65.10 | 10 | 100/72 |
| 55 | Styrallyl acetate | $C_{10}H_{12}O_2$ | 12.400 | 122.00>107.10 | 10 | 104.00>78.10 | 10 | 100/79 |
| 56 | α- terpineol (1. isomer) | $C_{10}H_{18}O$ | 12.407 | 93.00>77.10 | 14 | 93.00>91.10 | 10 | 100/78 |
| 57 | α -terpineol (2. isomer) | $C_{10}H_{18}O$ | 12.497 | 93.00>77.00 | 14 | 121.00>93.10 | 6 | 100/78 |
| 58 | Methyl salicylate | $C_8H_8O_3$ | 12.453 | 120.00>92.00 | 10 | 120.00>64.00 | 18 | 100/54 |
| 59 | Ethyl maltol | $C_7H_8O_3$ | 12.503 | 139.00>111.10 | 10 | 140.00>71.00 | 14 | 100/60 |
| 60 | Decanal | $C_{10}H_{20}O$ | 12.537 | 82.00>67.10 | 6 | 70.00>55.10 | 6 | 100/50 |
| 61 | Citral (1. isomer) | $C_{10}H_{16}O$ | 12.797 | 134.00>117.10 | 10 | 134.00>91.10 | 26 | 100/50 |
| 62 | Citronellol | $C_{10}H_{20}O$ | 12.823 | 95.00>67.10 | 10 | 123.00>81.10 | 6 | 100/75 |
| 63 | Nerol | $C_{10}H_{18}O$ | 12.853 | 93.00>77.10 | 10 | 93.00>51.20 | 22 | 100/75 |
| 64 | Cis-3-Hexenyl valerate | $C_{11}H_{20}O_2$ | 12.907 | 82.00>67.10 | 6 | 67.00>65.00 | 10 | 100/20 |
| 65 | Ethyl phenylacetate | $C_{10}H_{12}O_2$ | 13.027 | 91.00>65.10 | 18 | 164.00>91.10 | 14 | 100/32 |
| 66 | Carvone | $C_{10}H_{14}O$ | 13.067 | 82.00>54.10 | 6 | 108.00>93.10 | 10 | 100/47 |
| 67 | Linalyl acetate | $C_{12}H_{20}O_2$ | 13.133 | 93.00>77.00 | 14 | 93.00>91.10 | 6 | 100/44 |
| 68 | Geraniol | $C_{10}H_{18}O$ | 13.130 | 69.00>53.10 | 14 | 69.00>67.00 | 10 | 100/49 |
| 69 | Citral (2. isomer) | $C_{10}H_{16}O$ | 13.177 | 134.00>117.10 | 10 | 134.00>91.10 | 26 | 100/50 |
| 70 | L-menthyl acetate | $C_{12}H_{22}O_2$ | 13.565 | 95.00>67.10 | 10 | 95.00>55.10 | 14 | 100/72 |
| 71 | Theaspirane (1. isomer) | $C_{13}H_{22}O_2$ | 13.673 | 138.00>96.10 | 6 | 138.00>82.10 | 14 | 100/46 |
| 72 | Theaspirane (2. isomer) | $C_{13}H_{22}O_2$ | 13.827 | 138.00>96.10 | 6 | 138.00>82.00 | 14 | 100/50 |
| 73 | Capric acid | $C_{10}H_{20}O_2$ | 14.103 | 73.00>55.00 | 10 | 129.00>87.10 | 10 | 100/58 |
| 74 | Eugenol | $C_{10}H_{12}O_2$ | 14.153 | 164.00>149.10 | 10 | 164.00>104.10 | 14 | 100/36 |
| 75 | γ-nonalactone | $C_9H_{16}O$ | 14.181 | 85.00>57.10 | 6 | 85.00>83.00 | 26 | 100/20 |
| 76 | Hexyl hexanoate | $C_{12}H_{24}O_2$ | 14.318 | 117.00>89.10 | 10 | 117.00>75.00 | 10 | 100/45 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 77 | Methyl cinammate | $C_{10}H_{10}O_2$ | 14.363 | 131.00>103.10 | 10 | 131.00>77.10 | 26 | 100/64 |
| 78 | 3,4-dihydrocoumarin | $C_9H_8O_2$ | 14.413 | 148.00>120.10 | 10 | 148.00>91.10 | 26 | 100/74 |
| 79 | Vanillin | $C_8H_8O_3$ | 14.493 | 151.00>123.10 | 10 | 152.00>123.10 | 18 | 100/97 |
| 80 | Anisyl acetate | $C_{10}H_{12}O_3$ | 14.603 | 121.00>78.10 | 22 | 180.00>138.10 | 6 | 100/39 |
| 81 | β-damascone | $C_{13}H_{20}O$ | 14.610 | 123.00>81.10 | 10 | - | | 100/34 |
| 82 | α-Ionone | $C_{13}H_{20}O$ | 14.703 | 93.00>77.00 | 14 | 121.00>77.10 | 18 | 100/76 |
| 83 | Ethyl 3-methyl-3-phenylglycidate (1. isomer) | $C_{11}H_{12}O_3$ | 14.743 | 132.00>104.00 | 14 | 132.00>78.10 | 18 | 100/42 |
| 84 | Ethyl Vanillin | $C_9H_{10}O_3$ | 14.907 | 137.00>109.00 | 10 | 166.00>137.00 | 18 | 100/53 |
| 85 | Ethyl cinammate | $C_{11}H_{12}O_2$ | 14.940 | 131.00>103.10 | 10 | 131.00>77.10 | 22 | 100/49 |
| 86 | γ- decalactone | $C_{10}H_{18}O_2$ | 14.957 | 85.00>57.10 | 6 | 128.00>95.10 | 6 | 100/18 |
| 87 | β- ionone | $C_{13}H_{20}O$ | 15.107 | 177.00>147.10 | 22 | 177.00>162.10 | 10 | 100/33 |
| 88 | Phenenthyl isovalerate | $C_{13}H_{18}O_2$ | 15.113 | 105.00>79.10 | 11 | 85.00>57.10 | 6 | 100/15 |
| 89 | Cocal | $C_{13}H_{16}O$ | 15.117 | 117.00>115.10 | 10 | 117.00>91.10 | 18 | 100/79 |
| 90 | α,α-dimethylphenethyl butyrate | $C_{14}H_{20}O_2$ | 15.117 | 132.00>117.10 | 14 | 132.00>91.10 | 26 | 100/38 |
| 91 | δ-decalactone | $C_{10}H_{18}O_2$ | 15.153 | 99.00>71.10 | 6 | 99.00>55.10 | 14 | 100/45 |
| 92 | Ethyl 3-methyl-3-phenylglycidate (2. isomer) | $C_{11}H_{12}O_3$ | 15.340 | 132.00>104.10 | 10 | 132.00>78.10 | 18 | 100/42 |
| 93 | Raspberry ketone | $C_{10}H_{12}O_2$ | 15.473 | 107.00>77.00 | 14 | 164.00>107.10 | 14 | 100/42 |
| 94 | γ-undecalactone | $C_{11}H_{12}O_2$ | 15.613 | 85.00>57.10 | 6 | 85.00>70.10 | 6 | 100/12 |
| 95 | Hedione (1. isomer) | $C_{13}H_{22}O_3$ | 16.030 | 83.00>55.10 | 14 | 153.00>97.10 | 10 | 100/26 |
| 96 | Hedione (2. isomer) | $C_{13}H_{22}O_3$ | 16.173 | 83.00>55.10 | 14 | 153.00>97.10 | 10 | 100/26 |
| 97 | γ-dodecalactone | $C_{12}H_{22}O_2$ | 16.173 | 85.00>57.10 | 6 | 55.00>53.00 | 10 | 100/15 |
| 98 | δ-tetradecalactone | $C_{14}H_{26}O_2$ | 17.313 | 99.00>71.10 | 6 | 99.00>55.00 | 14 | 100/15 |

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446 ***Table 2***. *Categorization of target compounds into eight flavour categories*

| Compound name | Odour type according to Good Scents Company | Assigned flavour category |
|---|---|---|
| methyl heptenone, limonene, citral | Citrus | Fruity |
| δ-decalactone, γ-nonalactone | Coconut | |
| melonal | Melon | |
| ethyl butyrate, ethyl lactate (fruity), isopentyl acetate, benzaldehyde, ethyl heptanoate, β-damascone, γ-decalactone, ethyl 2-methylpropanoate, isopentyl isovalerate, diethyl succinate, isoamyl butyrate, ethyl caproate, ethyl 3-methyl-3-phenylglycidate, raspberry ketone, γ-undecalactone, γ-dodecalactone, 4-methyl-2-(1-methylethyl)-thiazole, diethyl malonate | Fruity | |
| 2-methylpyrazine, 2,3,5-trimethylpyrazine, 2,3,5,6-tetramethylpyrazine, 2,6-dimethylpyridine, | Nutty | Sweet |
| methyl cyclopentenolone, furaneol, maltol, ethyl maltol, 5-methylfurfural | Caramellic | |
| ethyl vanillin, vanillin | Vanilla | |
| 2,5-dimethylpyrazine, cocal | Chocolate | |
| anisyl acetate | Powdery | |
| furfural, leaf aldehyde, cis-3-hexenol, cis-3-hexenylacetate, trans-2-hexenol, styrallyl acetate, cis-3-hexenyl valerate, hexyl hexanoate, | Green | Miscellaneous |
| δ-tetradecalactone | Waxy | |
| capric acid | Fatty | |
| 2-acetylpyrrole | Musty | |
| 3-ethylpyridine | Tobacco | |
| furfuryl alcohol | Bready | |
| 2-acetylpyrazine, 2-acetylpyridine | Popcorn | |
| γ- butyrolactone | Creamy | |
| α-terpineol | Terpenic | |
| ethyl-3-methylthiopropionate | Sulforous | |
| tetrahydrolinalool, geranyl propionate, linalool, phenylethyl alcohol, benzyl acetate, 4'-methylacetophenone, benzyl alcohol, epoxydihydrolinalool, nerol, citronellol, geraniol, ethyl phenylacetate, β- ionone, phenenthyl isovalerate, α,α-dimethylphenethyl butyrate, hedione, α-ionone | Floral | Floral |
| 2-isopropyl-5-methylhex-2-enal, theaspirane, linalyl acetate, γ- valeroactone, n-hexanol | Herbal | Herbal |
| γ- hexalactone, 3,4-dihydrocoumarin | Tonka | |
| menthone, carvone, methyl salicylate | Minty | Menthol |
| L-menthylacetate, menthol | Mentholic | |
| eugenol | Spicy | Spicy |
| methyl cinammate, ethyl cinammate | Balsamic | Alcoholic |
| decanal | Aldehydic | |
| 1-amylalcohol | Fermented | |

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***Table 3.*** *Calculated numerical values of parameters describing calibration curves in solvent and matrix, LOD, LOQ, correlation coefficient of method for quantification of flavouring additives in e-cigarette refill solutions.*

| Compound name | Calibration curve range [ng/mL) | Solvent calibration curve | | | Matrix matched calibration curve | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 7 points, n=3 | a | b | r | a | b | $S_a$ | $S_b$ | LOD | LOQ | r | ME [%] |
| Ethyl 2-methylpropanoate | 50-5000 | 0.000599 | -0.0050 | 0.9932 | 0.0003243 | 0.0012 | 0.0000056 | 0.0027 | 28 | 83 | 0.9901 | -45.9 |
| 1-amylalcohol | 100-5000 | 0.001608 | 0.009 | 0.9937 | 0.0007091 | 0.0127 | 0.0000067 | 0.0048 | 22 | 66 | 0.9917 | -55.9 |
| Ethyl butyrate | 100-5000 | 0.000816 | 0.004 | 0.9956 | 0.000487 | 0.008 | 0.000020 | 0.014 | 95 | 284 | 0.9901 | -40.4 |
| Ethyl lactate | 100-5000 | 0.0001198 | -0.0058 | 0.9939 | 0.0001035 | 0.0003 | 0.0000028 | 0.0020 | 63 | 188 | 0.9927 | -13.6 |
| 2-methylpyrazine | 100-5000 | 0.000644 | 0.065 | 0.9912 | 0.000858 | -0.043 | 0.000016 | 0.012 | 45 | 134 | 0.9901 | 33.2 |
| Furfural | 50-5000 | 0.0002939 | -0.0026 | 0.9930 | 0.0002795 | -0.0047 | 0.0000028 | 0.0013 | 16 | 48 | 0.9938 | -4.9 |
| Leaf aldehyde | 100-5000 | 0.0002156 | -0.0090 | 0.9858 | 0.0001849 | -0.0070 | 0.0000036 | 0.0026 | 46 | 137 | 0.9921 | -14.2 |
| Furfuryl alcohol | 250-5000 | 0.0004333 | -0.0029 | 0.9979 | 0.000360 | 0.001 | 0.000011 | 0.011 | 105 | 316 | 0.9925 | -16.9 |
| Cis-3-hexenol | 50-5000 | 0.000616 | -0.0012 | 0.9915 | 0.0006961 | -0.0160 | 0.0000091 | 0.0044 | 21 | 63 | 0.9963 | 13.0 |
| Trans-2-hexanol | 50-5000 | 0.000407 | -0.0046 | 0.9911 | 0.0004258 | -0.0040 | 0.0000054 | 0.0026 | 20 | 61 | 0.9968 | 4.5 |
| n-Hexanol | 100-5000 | 0.0000756 | -0.0009 | 0.9986 | 0.00006575 | -0.00063 | 0.00000090 | 0.00064 | 32 | 96 | 0.9915 | -13.0 |
| Isopentyl acetate | 100-5000 | 0.0004756 | -0.0001 | 0.9933 | 0.000423 | -0.0080 | 0.000013 | 0.0095 | 74 | 222 | 0.9901 | -11.0 |
| 2,6-dimethylpyridine | 50-5000 | 0.000713 | -0.0127 | 0.9965 | 0.0005817 | 0.0042 | 0.0000099 | 0.0048 | 27 | 82 | 0.9938 | -18.4 |
| 2,5-dimethylpyrazine | 50-5000 | 0.000604 | -0.0123 | 0.9910 | 0.0005750 | -0.0104 | 0.0000059 | 0.0029 | 16 | 49 | 0.9950 | -4.8 |
| γ-butyrolactone | 50-5000 | 0.0002910 | -0.0015 | 0.9979 | 0.0003490 | 0.0005 | 0.0000027 | 0.0013 | 13 | 38 | 0.9986 | 19.9 |
| γ-valeroactone | 50-5000 | 0.0002401 | -0.0009 | 0.9975 | 0.0002885 | -0.0004 | 0.0000035 | 0.0017 | 19 | 58 | 0.9976 | 20.2 |
| 3-ethylpyridine | 50-5000 | 0.001819 | -0.0299 | 0.9981 | 0.002057 | -0.0412 | 0.000017 | 0.0082 | 13 | 39 | 0.9978 | 13.1 |
| Benzaldehyde | 50-5000 | 0.001642 | 0.0186 | 0.9962 | 0.001815 | 0.0325 | 0.000011 | 0.0051 | 9 | 28 | 0.9964 | 10.5 |
| 5-methylfurfural | 50-5000 | 0.001458 | -0.0062 | 0.9989 | 0.0016206 | -0.0080 | 0.0000092 | 0.0045 | 9 | 27 | 0.9952 | 11.1 |
| Methyl heptenone | 50-5000 | 0.0003756 | -0.0020 | 0.9989 | 0.0003784 | -0.00355 | 0.0000019 | 0.00094 | 8 | 25 | 0.9989 | 0.7 |
| Ethyl caproate | 50-5000 | 0.000947 | 0.001 | 0.9926 | 0.000902 | -0.0176 | 0.000010 | 0.0050 | 18 | 55 | 0.9950 | -4.8 |
| 2,3,5-trimethylpyrazine | 50-5000 | 0.0009093 | -0.0109 | 0.9954 | 0.000946 | -0.0036 | 0.000012 | 0.0058 | 20 | 60 | 0.9958 | 4.1 |
| Cis-3-hexenylacetate | 50-5000 | 0.001670 | -0.0275 | 0.9921 | 0.001527 | -0.0178 | 0.000016 | 0.0076 | 16 | 49 | 0.9924 | -8.5 |
| 4-methyl-2-(1-methylethyl)-thiazole | 50-5000 | 0.001158 | -0.0213 | 0.9970 | 0.0010614 | -0.0144 | 0.0000089 | 0.0043 | 13 | 40 | 0.9973 | -8.3 |
| 2-acetylpyrazine | 50-5000 | 0.0007023 | -0.0042 | 0.9990 | 0.0008119 | -0.0032 | 0.0000052 | 0.0026 | 10 | 31 | 0.9989 | 15.6 |
| Methyl cyclopentenolone | 50-5000 | 0.001056 | -0.062 | 0.9922 | 0.001692 | 0.0504 | 0.000017 | 0.0082 | 16 | 48 | 0.9982 | 60.3 |
| Limonene | 50-5000 | 0.0005135 | -0.0058 | 0.9985 | 0.0005951 | -0.0016 | 0.0000026 | 0.0013 | 7 | 21 | 0.9984 | 15.9 |
| 2-acetylpyridine | 50-5000 | 0.0012104 | -0.0062 | 0.9992 | 0.001305 | -0.008 | 0.000025 | 0.012 | 31 | 93 | 0.9956 | 7.8 |
| Benzyl alcohol | 50-5000 | 0.001917 | -0.0116 | 0.9986 | 0.002193 | -0.038 | 0.000034 | 0.017 | 25 | 76 | 0.9986 | 14.4 |
| Melonal | 50-5000 | 0.002185 | -0.0034 | 0.9990 | 0.002289 | -0.013 | 0.000021 | 0.010 | 15 | 44 | 0.9981 | 4.7 |
| Furaneol | 250-5000 | 0.000172 | -0.041 | 0.9820 | 0.0003297 | -0.0200 | 0.0000059 | 0.0063 | 63 | 188 | 0.9969 | 91.4 |
| | 50-5000* | | | | 0.0003212 | -0,0046 | 0,0000054 | 0.0026 | 27 | 81 | 0.9966 | |
| γ-hexalactone | 50-5000 | 0.001728 | -0.003 | 0.9956 | 0.001703 | -0.0015 | 0.000012 | 0.0059 | 11 | 34 | 0.9985 | -1.5 |
| Isoamyl butyrate | 50-5000 | 0.0000966 | -0.00011 | 0.9981 | 0.0000948 | -0.0004 | 0.0000011 | 0.0005 | 18 | 54 | 0.9973 | -1.9 |
| 2-acetylpyrrole | 50-5000 | 0.003936 | -0.0452 | 0.9982 | 0.005048 | -0.007 | 0.000073 | 0.036 | 23 | 70 | 0.9940 | 28.2 |
| Diethyl malonate | 50-5000 | 0.0011331 | -0.0124 | 0.9986 | 0.001304 | -0.0030 | 0.000011 | 0.0056 | 14 | 42 | 0.9984 | 15.1 |
| 2,3,5,6-tetramethylpyrazine | 50-5000 | 0.0018555 | 0.028 | 0.9996 | 0.0020950 | -0.0148 | 0.0000024 | 0.0050 | 8 | 24 | 0.9997 | 12.9 |
| Epoxydihydrolinalool (2 isomers) | 50-5000 | 0.0011321 | -0.0049 | 0.9994 | 0.0012237 | -0.0031 | 0.0000054 | 0.0026 | 7 | 21 | 0.9993 | 8.1 |
| Ethyl heptanoate | 50-5000 | 0.001600 | -0.0183 | 0.9971 | 0.0015517 | -0.0303 | 0.0000071 | 0.0035 | 7 | 22 | 0.9974 | -3.0 |
| Tetrahydrolinalool | 50-5000 | 0.002716 | 0.006 | 0.9987 | 0.002714 | -0.0156 | 0.000013 | 0.0065 | 8 | 24 | 0.9984 | -0.1 |
| Geranyl propionate | 50-5000 | 0.002267 | -0.0145 | 0.9984 | 0.002252 | -0.0336 | 0.000012 | 0.0058 | 8 | 25 | 0.9977 | -0.7 |
| Linalool | 50-5000 | 0.0011758 | -0.0071 | 0.9994 | 0.0012632 | 0.0000 | 0.0000026 | 0.0013 | 3 | 10 | 0.9992 | 7.4 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ethyl-3-methylthiopropionate | 50-5000 | 0.0011210 | -0.0099 | 0.9986 | 0.0011870 | -0.0018 | 0.0000055 | 0.0027 | 7 | 22 | 0.9995 | 5.9 |
| Isopentyl isovalerate | 50-5000 | 0.002289 | -0.010 | 0.9954 | 0.002074 | -0.006 | 0.000029 | 0.014 | 22 | 67 | 0.9952 | -9.4 |
| Maltol | 500-5000 | 0.000455 | -0.253 | 0.9968 | 0.000923 | -0.132 | 0.000034 | 0.051 | 182 | 545 | 0.9941 | 102.7 |
| | 100-5000* | | | | 0.000892 | -0.073 | 0.000028 | 0.020 | 74 | 221 | 0.9928 | |
| Phenylethyl alcohol | 50-5000 | 0.002574 | -0.025 | 0.9983 | 0.002966 | -0.084 | 0.000063 | 0.031 | 34 | 102 | 0.9850 | 15.2 |
| 2-Isopropyl-5-methylhex-2-enal (2 isomers) | 100-5000 | 0.0002311 | -0.0030 | 0.9981 | 0.00023141 | -0.00127 | 0.00000087 | 0.00061 | 9 | 26 | 0.9981 | 0.1 |
| Benzyl acetate | 50-5000 | 0.002445 | -0.0189 | 0.9994 | 0.002646 | 0.0007 | 0.000015 | 0.0075 | 9 | 28 | 0.9994 | 8.2 |
| Menthone | 50-5000 | 0.0009565 | -0.0098 | 0.9990 | 0.0009316 | -0.0003 | 0.0000027 | 0.0013 | 5 | 14 | 0.9996 | -2.6 |
| Menthol | 50-5000 | 0.0003996 | 0.00051 | 0.9988 | 0.0004315 | -0.0078 | 0.0000024 | 0.0049 | 37 | 112 | 0.9997 | 8.0 |
| Diethyl succinate | 50-5000 | 0.0030283 | -0.0417 | 0.9987 | 0.003436 | -0.030 | 0.000018 | 0.038 | 36 | 109 | 0.9993 | 13.5 |
| 4'-methylacetophenone | 50-5000 | 0.004934 | -0.0331 | 0.9992 | 0.005419 | -0.0003 | 0.00002 | 0.0107 | 7 | 20 | 0.9995 | 9.8 |
| Styrallyl acetate | 50-5000 | 0.0023081 | -0.0139 | 0.9994 | 0.002477 | 0.0009 | 0.00001 | 0.0053 | 7 | 21 | 0.9995 | 7.3 |
| Alpha terpineol (2 isomers) | 50-5000 | 0.002120 | -0.0003 | 0.9992 | 0.001357 | 0.0043 | 0.00001 | 0.0049 | 12 | 36 | 0.9990 | -36.0 |
| Methyl salicylate | 50-5000 | 0.003842 | -0.0383 | 0.9992 | 0.0041607 | -0.0032 | 0.0000086 | 0.0042 | 3 | 10 | 0.9997 | 8.3 |
| Ethyl maltol | 500-5000 | 0.000147 | -0.084 | 0.9982 | 0.000479 | -0.065 | 0.000017 | 0.026 | 180 | 541 | 0.9941 | 227.2 |
| | 100-5000* | | | | 0.000462 | -0.0308 | 0.000014 | 0.0096 | 69 | 207 | 0.9934 | |
| Decanal | 50-5000 | 0.0006632 | -0.0005 | 0.9951 | 0.0006257 | 0.0060 | 0.0000021 | 0.0010 | 5 | 16 | 0.9976 | -5.7 |
| Citronellol | 50-5000 | 0.0005009 | -0.0082 | 0.9987 | 0.0005398 | 0.0033 | 0.0000022 | 0.0011 | 7 | 20 | 0.9992 | 7.8 |
| Nerol | 50-5000 | 0.0005895 | -0.0128 | 0.9952 | 0.0006730 | -0.0051 | 0.0000062 | 0.0030 | 15 | 44 | 0.9954 | 14.2 |
| Cis-3-Hexenyl valerate | 50-5000 | 0.003485 | -0.035 | 0.9986 | 0.003346 | -0.007 | 0.000028 | 0.014 | 13 | 40 | 0.9971 | -4.0 |
| Ethyl phenylacetate | 50-5000 | 0.003604 | -0.018 | 0.9976 | 0.0034696 | 0.0020 | 0.0000085 | 0.0041 | 4 | 12 | 0.9972 | -3.7 |
| Carvone | 50-5000 | 0.001865 | -0.0107 | 0.9981 | 0.0020069 | -0.0054 | 0.0000098 | 0.0048 | 8 | 24 | 0.9991 | 7.6 |
| Linalyl acetate | 50-5000 | 0.001408 | -0.030 | 0.9969 | 0.0021123 | -0.0189 | 0.0000079 | 0.0038 | 6 | 18 | 0.9997 | 50.0 |
| Geraniol | 100-5000 | 0.00002593 | -0.00016 | 0.9963 | 0.00003139 | -0.00009 | 0.00000025 | 0.00018 | 19 | 56 | 0.9992 | 21.1 |
| Citral | 50-5000 | 0.0002970 | -0.00333 | 0.9987 | 0.0003180 | 0.00110 | 0.0000019 | 0.00093 | 10 | 29 | 0.9993 | 7.1 |
| L-menthyl acetate | 50-5000 | 0.0014619 | -0.0192 | 0.9943 | 0.001324 | 0.0009 | 0.000015 | 0.0073 | 18 | 54 | 0.9974 | -9.4 |
| Theaspirane (2 isomers) | 50-5000 | 0.002093 | -0.009 | 0.9941 | 0.001945 | -0.012 | 0.000030 | 0.015 | 25 | 74 | 0.9928 | -7.1 |
| Capric acid | 1000-5000 | 0.000192 | -0.203 | 0.9981 | 0.000305 | -0.161 | 0.000024 | 0.052 | 562 | 1686 | 0.9896 | 58.9 |
| | 500-5000* | | | | 0.000284 | -0.083 | 0.000015 | 0.023 | 272 | 816 | 0.9900 | |
| Eugenol | 50-5000 | 0.0013987 | -0.0340 | 0.9979 | 0.001599 | -0.0022 | 0.000013 | 0.0064 | 13 | 40 | 0.9988 | 14.3 |
| γ-nonalactone | 50-5000 | 0.002130 | -0.0288 | 0.9983 | 0.002269 | -0.0052 | 0.000017 | 0.0082 | 12 | 36 | 0.9987 | 6.5 |
| Hexyl hexanoate | 50-5000 | 0.0005572 | -0.0045 | 0.9972 | 0.0005117 | 0.0001 | 0.0000035 | 0.0017 | 11 | 33 | 0.9971 | -8.2 |
| Methyl cinammate | 50-5000 | 0.005020 | -0.065 | 0.9971 | 0.005491 | -0.022 | 0.000034 | 0.016 | 10 | 30 | 0.9991 | 9.4 |
| 3,4-dihydrocoumarin | 50-5000 | 0.003662 | -0.051 | 0.9974 | 0.004004 | 0.011 | 0.000032 | 0.015 | 13 | 38 | 0.9987 | 9.3 |
| Vanillin | 100-5000 | 0.001094 | -0.101 | 0.9925 | 0.001948 | -0.048 | 0.000029 | 0.020 | 34 | 103 | 0.9967 | 78.0 |
| Anisyl acetate | 50-5000 | 0.002741 | -0.0492 | 0.9981 | 0.002956 | -0.014 | 0.000023 | 0.011 | 13 | 38 | 0.9988 | 7.8 |
| β-damascone | 50-5000 | 0.0004760 | -0.0044 | 0.9970 | 0.0004919 | -0.0019 | 0.0000023 | 0.0011 | 8 | 23 | 0.9994 | 3.3 |
| α-Ionone | 50-5000 | 0.001801 | -0.0183 | 0.9970 | 0.0018430 | -0.0082 | 0.0000083 | 0.0040 | 7 | 22 | 0.9992 | 2.3 |
| Ethyl Vanillin | 100-5000 | 0.002779 | -0.261 | 0.9957 | 0.00431 | -0.191 | 0.00013 | 0.091 | 70 | 209 | 0.9928 | 54.9 |
| γ-decalactone | 50-5000 | 0.002306 | -0.037 | 0.9981 | 0.002276 | -0.0102 | 0.000015 | 0.0072 | 10 | 31 | 0.9985 | -1.3 |
| Ethyl cinammate | 50-5000 | 0.005316 | -0.086 | 0.9983 | 0.005538 | -0.035 | 0.000040 | 0.019) | 13 | 40 | 0.9990 | -4.0 |
| β-ionone | 50-5000 | 0.0011193 | -0.0146 | 0.9970 | 0.0011171 | -0.0045 | 0.0000048 | 0.0023 | 7 | 20 | 0.9993 | -0.2 |
| Phenenthyl isovalerate | 50-5000 | 0.001035 | -0.0090 | 0.9964 | 0.0010068 | -0.0016 | 0.0000093 | 0.0045 | 15 | 45 | 0.9985 | -2.8 |
| Cocal | 50-5000 | 0.001435 | -0.0168 | 0.9964 | 0.0014030 | 0.0017 | 0.0000084 | 0.0041 | 10 | 29 | 0.9980 | -2.2 |
| α,α-dimethylphenethyl butyrate | 50-5000 | 0.003162 | -0.031 | 0.9973 | 0.003159 | -0.0076 | 0.000017 | 0.0083 | 9 | 26 | 0.9992 | -0.1 |
| δ-decalactone | 50-5000 | 0.005330 | -0.120 | 0.9957 | 0.004986 | 0.008 | 0.000042 | 0.021 | 14 | 41 | 0.9982 | -6.4 |
| Ethyl 3-methyl-3-phenylglycidate (2 isomers) | 50-5000 | 0.001881 | -0.0490 | 0.9975 | 0.002143 | -0.0187 | 0.000016 | 0.0076 | 12 | 35 | 0.9988 | 14.0 |
| Raspberry ketone | 50-5000 | 0.004128 | -0.244 | 0.9942 | 0.004357 | 0.017 | 0.000056 | 0.027 | 21 | 62 | 0.9961 | 5.6 |
| γ-undecalactone | 50-5000 | 0.002396 | -0.043 | 0.9964 | 0.002262 | -0.0098 | 0.000015 | 0.0074 | 11 | 32 | 0.9986 | -5.6 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hedione (2 isomers) | 50-5000 | 0.002589 | -0.064 | 0.9955 | 0.002344 | 0.0043 | 0.000020 | 0.0097 | 14 | 41 | 0.9983 | -9.5 |
| γ-dodecalactone | 50-5000 | 0.002238 | -0.058 | 0.9953 | 0.001985 | 0.032 | 0.000069 | 0.034 | 56 | 168 | 0.9965 | -11.3 |
| δ-tetradecalactone | 50-5000 | 0.005989 | -0.246 | 0.9960 | 0.0053 | -0.068 | 0.0053 | -0.068 | 42 | 127 | 0.9971 | -12.2 |

* Due to the smaller detector response in the solvent calibration solutions compared to those prepared in the matrix, it was decided to use the calibration curve equation in this range for quantitative analysis

*where:* $S_a$ *– standard deviation of slope,* $S_b$ *– standard deviation of intercept, r – correlation coefficient, LOD – limit of detection, LOQ – limit of quantitation, n – number of measurements, ME – matrix effect*

*List of figures:*

***Figure 1.*** *Example of chromatograms obtained for real samples (Strawberry - brand A and Menthol- brand B) and for standard mixture (500 ng/mL each) the peak numbers correspond to the number given in Table 1*

***Figure 2.*** *Number of flavour chemicals in investigated e-liquid samples. Total number of identified compounds in each sample is shown above the bars and represents the number of flavour additives. The colours represent the eight different flavour categories. Segment on the bars represent the percentage of the total flavour chemicals number. The letters: A,B,C,D,E indicate the brands*

***Figure 3.*** *Concentration of flavour chemicals in investigated e-liquid samples. Total number of identified compounds in each sample is shown above the bars and represents the number of flavour additives. The colours represent the eight different flavour categories. Segment on the bars represent the percentage of the total flavour chemicals concentration. The letters: A,B,C,D,E indicate the brands*

***Figure 4.*** *Venn diagrams present shared and unique flavour additives identified in investigated e-liquid samples*

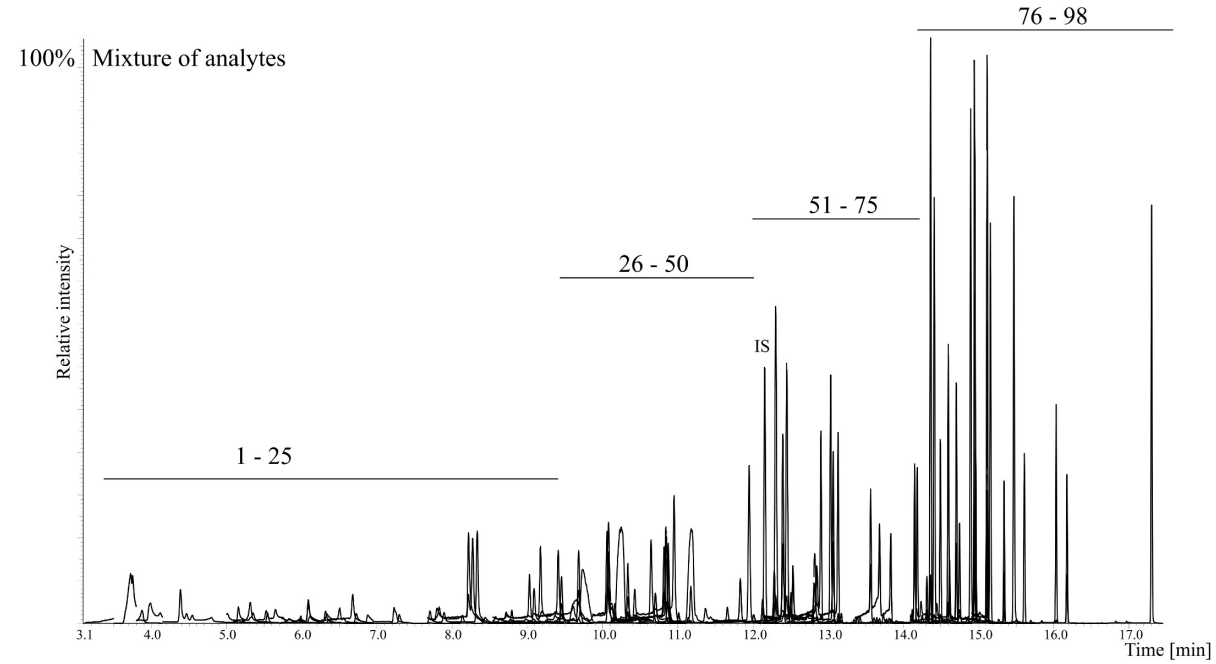
***Figure 5.*** *Scatter plot showing the distribution levels of common compounds within given flavours*

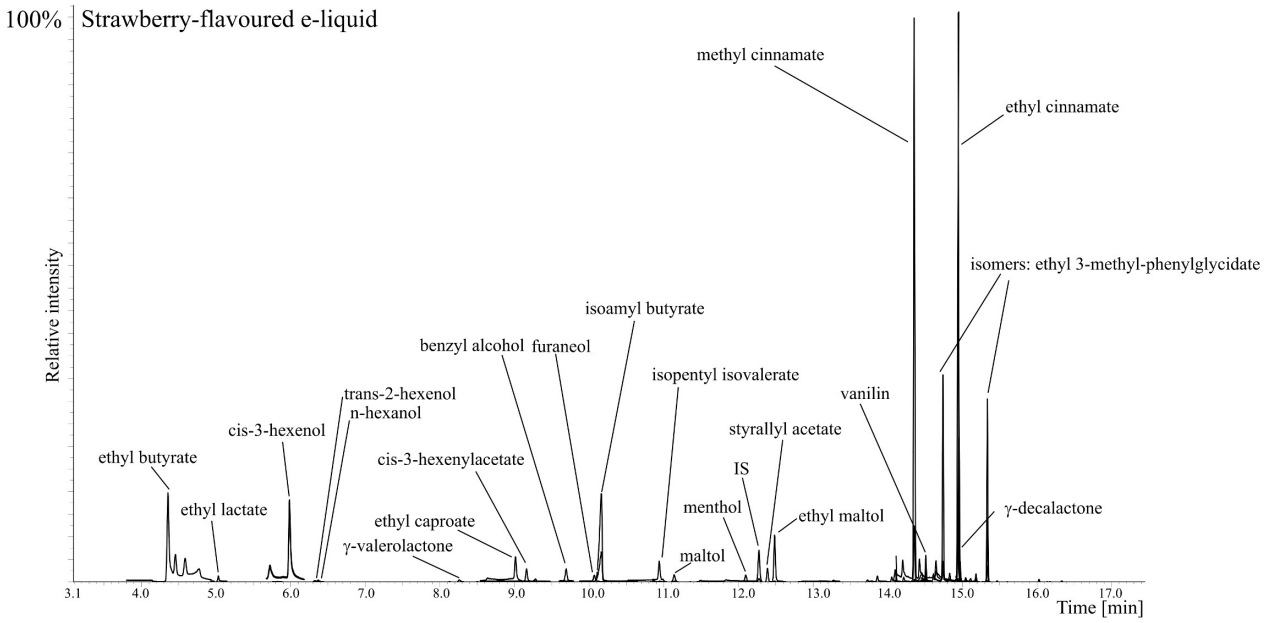
*List of supplementary material:*

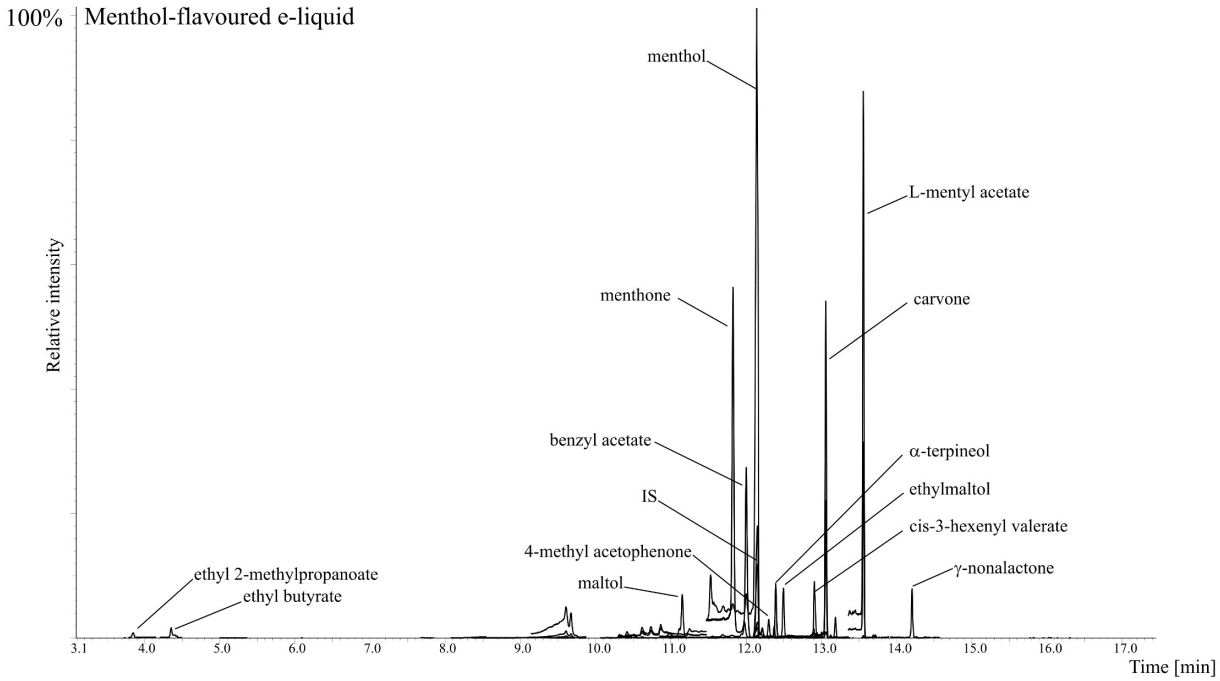
***Table S1.*** *Repeatability and precision data of developed method*

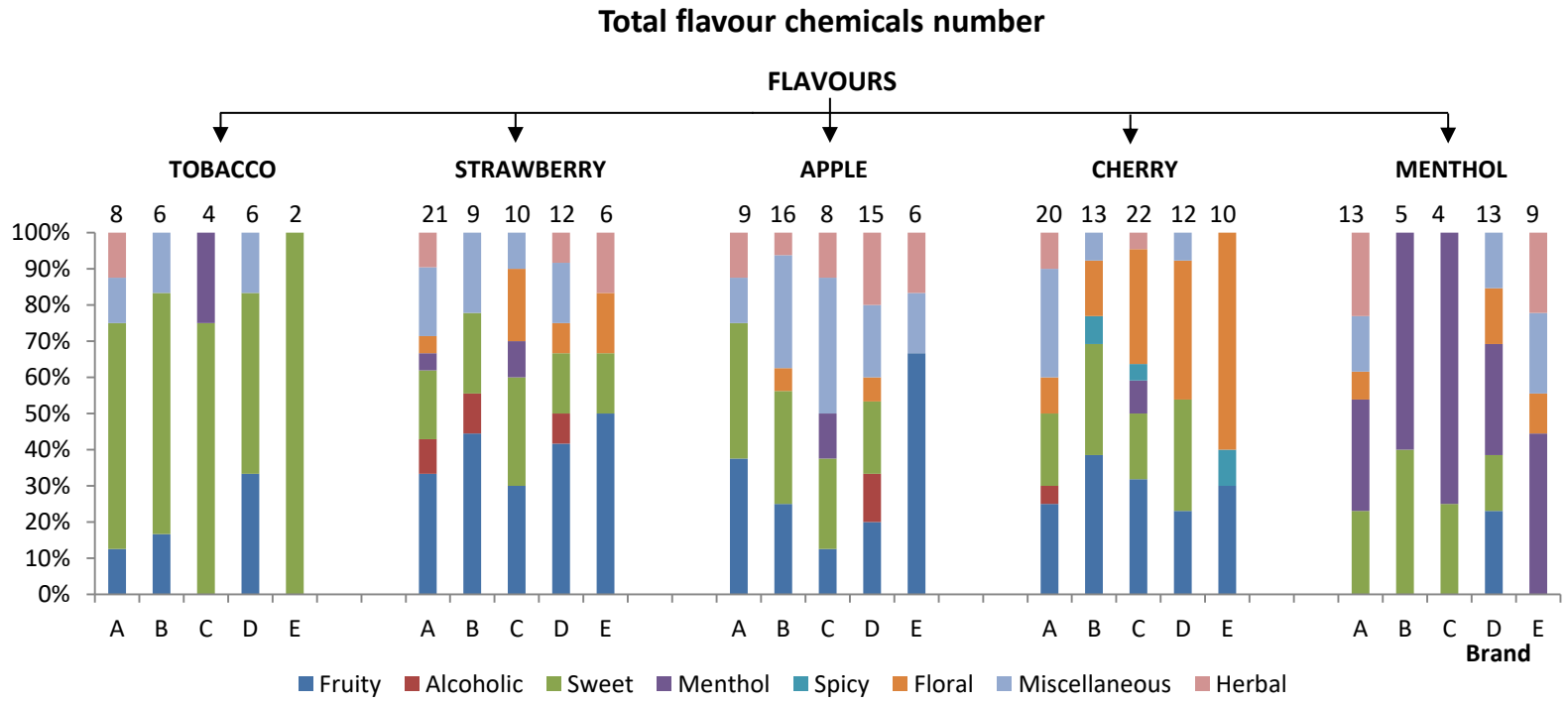
***Table S2.*** *Concentrations (mg/mL ± SD) of determinated flavour chemicals in investigated e – liquid samples*

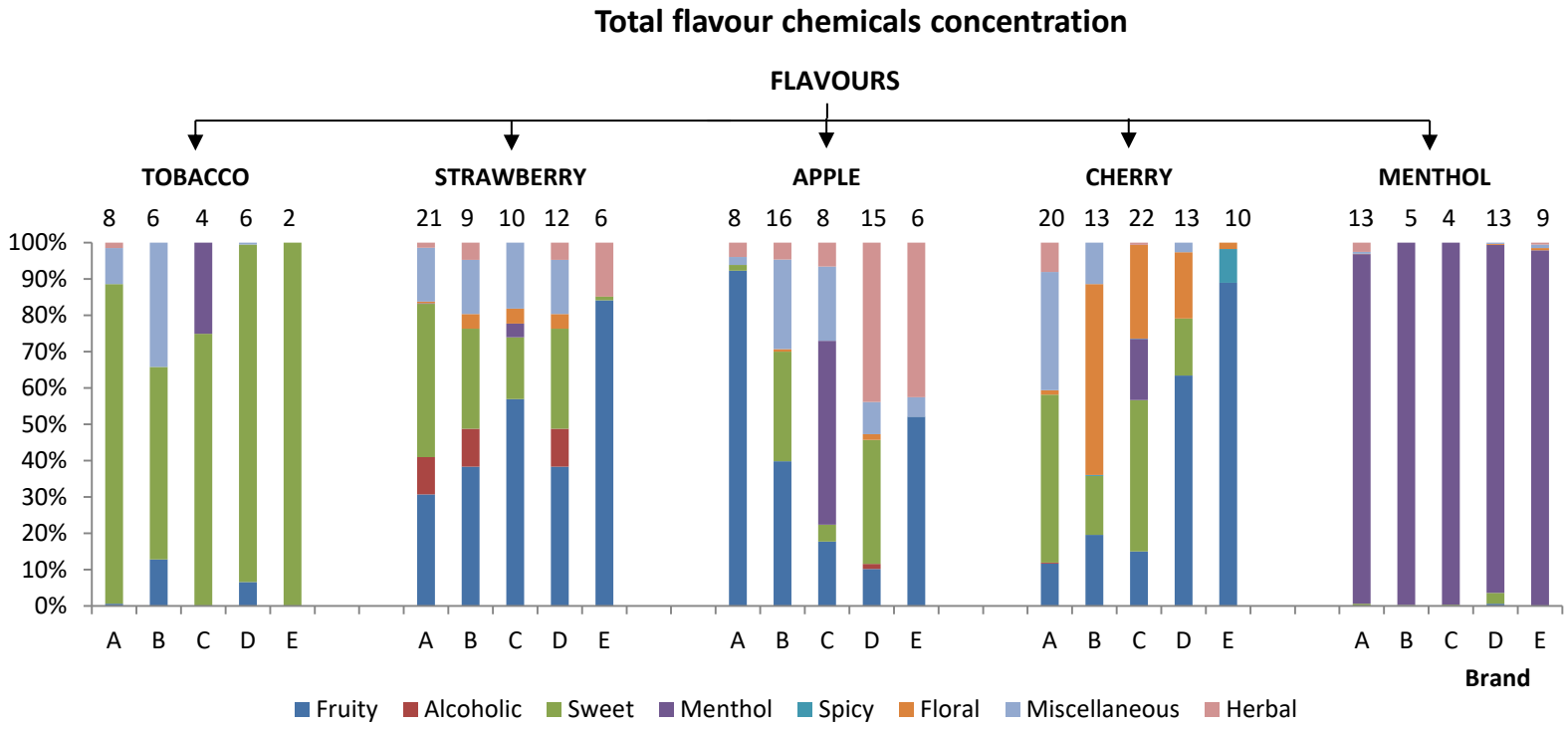
***Figure S1.*** *Comparison of total flavour concentration and price among investigated brand and flavours. Prices are given for bottle of e-liquid of volume 10 mL.*


100%
Mixture of analytes
Relative intensity
76 - 98
51 - 75
26 - 50
IS
1 - 25
3.1
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
Time [min]

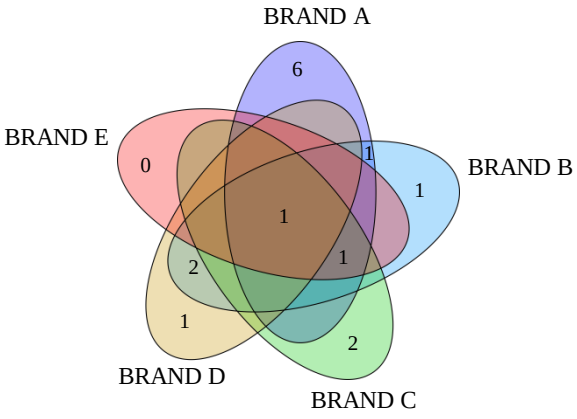

100%
Strawberry-flavoured e-liquid
Relative intensity
methyl cinnamate
ethyl cinnamate
isomers: ethyl 3-methyl-phenylglycidate
isoamyl butyrate
benzyl alcohol
furaneol
isopentyl isovalerate
vanilin
trans-2-hexenol
n-hexanol
cis-3-hexenol
styrallyl acetate
ethyl butyrate
cis-3-hexenylacetate
IS
menthol
ethyl lactate
ethyl caproate
ethyl maltol
γ-decalactone
γ-valerolactone
maltol
3.1
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
Time [min]


100%
Menthol-flavoured e-liquid
Relative intensity
menthol
L-mentyl acetate
menthone
carvone
benzyl acetate
α-terpineol
IS
ethylmaltol
cis-3-hexenyl valerate
4-methyl acetophenone
γ-nonalactone
maltol
ethyl 2-methylpropanoate
ethyl butyrate
3.1
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
Time [min]

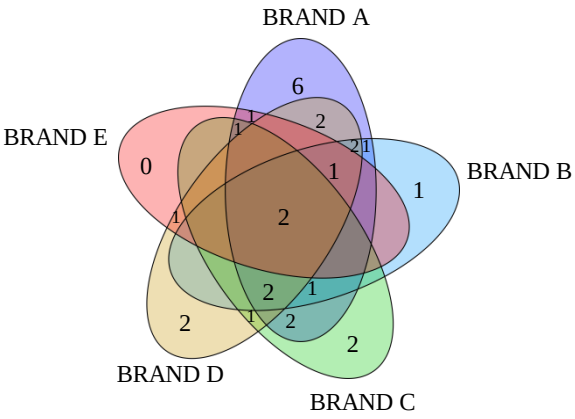




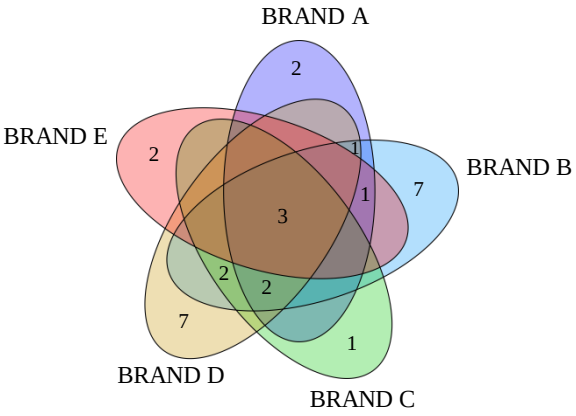
## TOBACCO



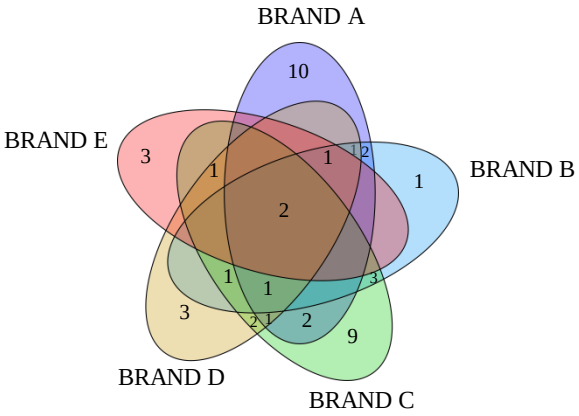

## STRAWBERRY



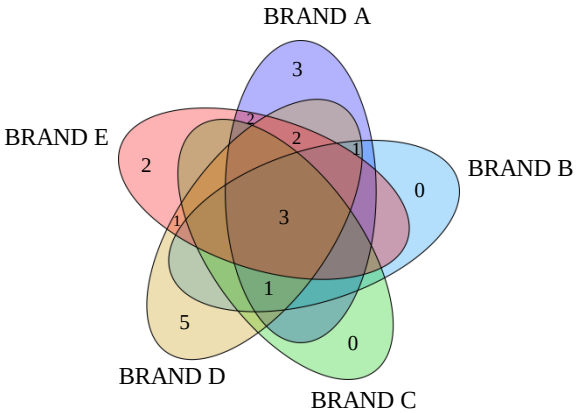

## APPLE




## CHERRY

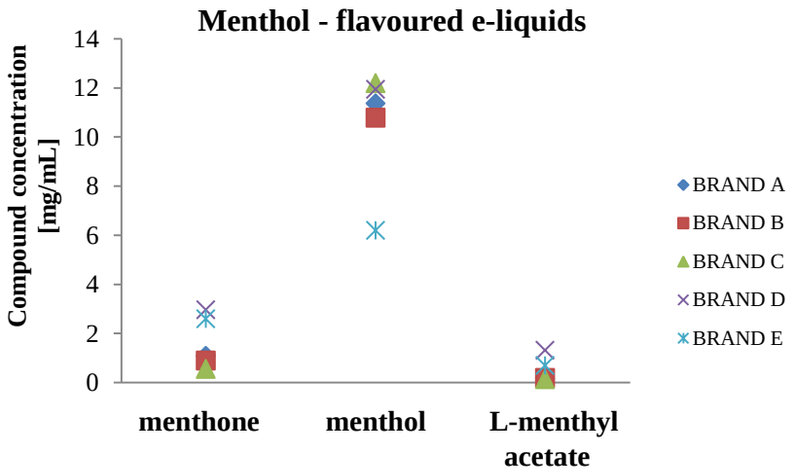


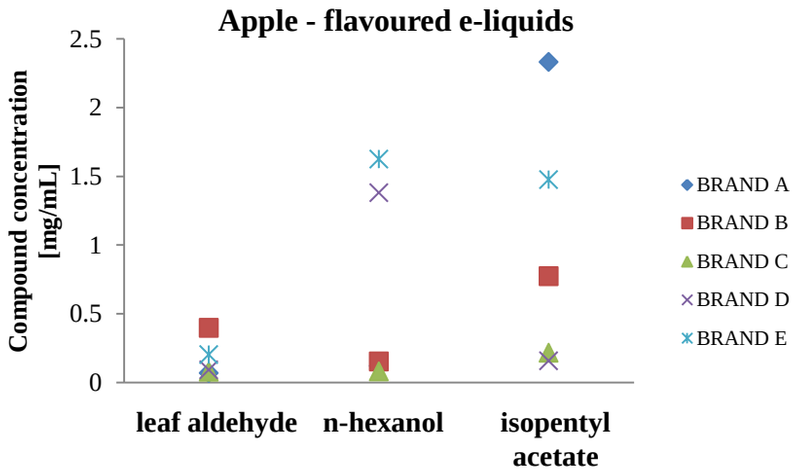

## MENTHOL

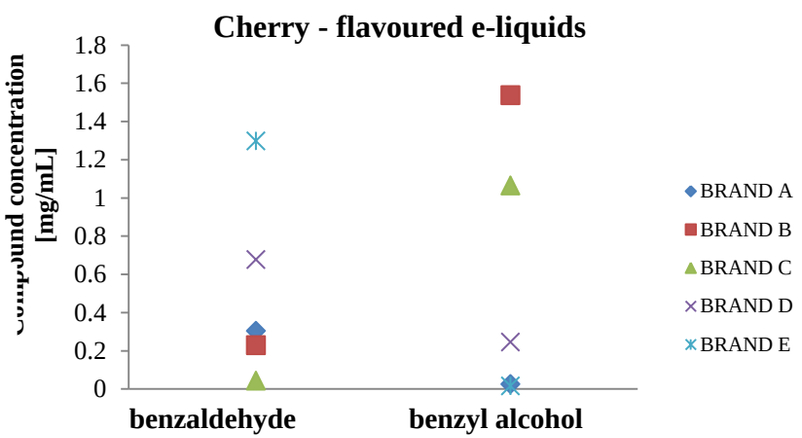


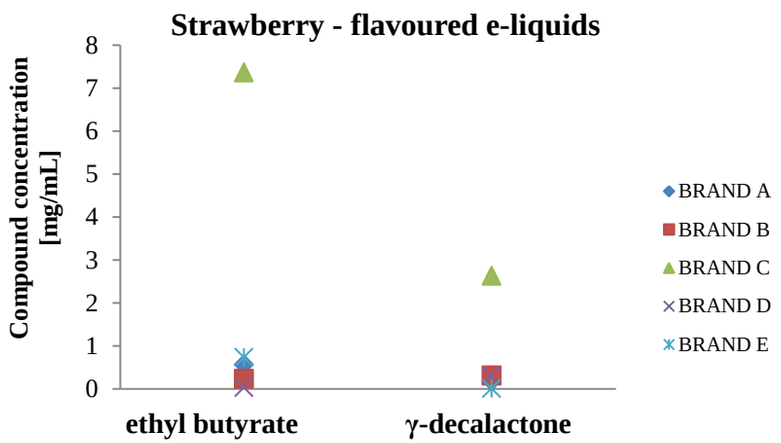

**Legend**

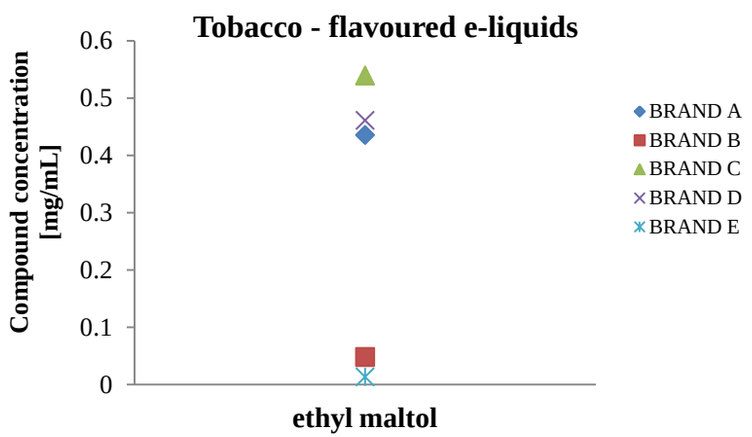
| Flavour | Common flavour chemicals (for 100% samples) | Common flavour chemicals (for 80 % samples) |
|---|---|---|
| TOBACCO | Ethyl maltol | - |
| STRAWBERRY | Ethyl butyrate, γ – decalactone | cis-3-hexenol, Ethyl maltol Ethyl caproate |
| APPLE | Leaf aldehyde, N-hexanol, Isopentyl acetate | Ethyl maltol, Vanillin |
| CHERRY | Benzaldehyde, Benzyl alcohol | Ethyl maltol, Vanillin |
| MENTHOL | Menthol, Menthone, L-menthylacetate | Ethyl maltol |



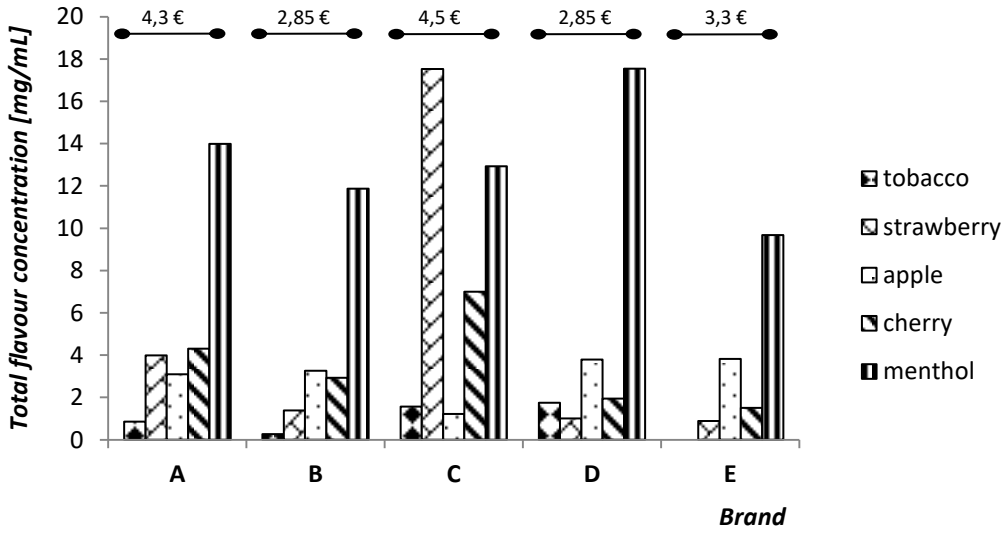


**Table S1** *Repeatability and precision data of developed method*

| Compound name | Repeatability and precision (n=3) | | | | | | | | | Intermediate precision (n=9) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Spiking level | | | | | | | | | | | |
| | 100×10$^{-6}$ mg/mL | | | 800×10$^{-6}$ mg/mL | | | 4000×10$^{-6}$ mg/mL | | | 800×10$^{-6}$ mg/mL | | |
| | Mean concentration [×10$^{-6}$ mg/mL ] | Accuracy [%] | CV [%] | Mean concentration [×10$^{-6}$ mg/mL] | Accuracy [%] | CV [%] | Mean concentration [×10$^{-6}$ mg/mL ] | Accuracy [%] | CV [%] | Mean concentration [×10$^{-6}$ mg/mL] | Accuracy [%] | CV [%] |
| Ethyl 2-methylpropanoate | 100 | 100 | 9 | 709 | 89 | 5 | 4182 | 105 | 5 | 727 | 92 | 10 |
| 1-amylalcohol | 103 | 103 | 4 | 823 | 103 | 8 | 4302 | 108 | 0.5 | 722 | 106 | 2 |
| Ethyl butyrate | 92 | 92 | 4 | 751 | 93 | 3 | 3732 | 104 | 4 | 775 | 88 | 8 |
| Ethyl lactate | 89 | 89 | 8 | 732 | 92 | 7 | 3925 | 98 | 9 | 860 | 98 | 2 |
| 2-methylpyrazine | 102 | 102 | 0.7 | 866 | 108 | 3 | 3696 | 92 | 6 | 738 | 98 | 4 |
| Furfural | 107 | 107 | 12 | 848 | 106 | 6 | 3752 | 94 | 10 | 729 | 112 | 4 |
| Leaf aldehyde | 104 | 104 | 0.8 | 895 | 112 | 6 | 4034 | 101 | 10 | 845 | 106 | 4 |
| Furfuryl alcohol* | 323 | 108 | 5 | 867 | 108 | 11 | 4399 | 110 | 1 | 842 | 111 | 7 |
| Cis-3-hexenol | 106 | 106 | 5 | 815 | 102 | 2 | 4112 | 103 | 4 | 773 | 111 | 7 |
| Trans-2-hexenol | 89 | 89 | 13 | 783 | 98 | 4 | 4101 | 103 | 8 | 771 | 97 | 9 |
| n-Hexanol | 93 | 93 | 4 | 790 | 99 | 11 | 3610 | 90 | 9 | 768 | 110 | 6 |
| Isopentyl acetate | 92 | 92 | 2 | 855 | 107 | 9 | 4137 | 103 | 12 | 788 | 91 | 10 |
| 2,6-dimethylpyridine | 100 | 100 | 10 | 751 | 94 | 4 | 3787 | 95 | 6 | 841 | 99 | 7 |
| 2,5-dimethylpyrazine | 100 | 100 | 6 | 851 | 106 | 5 | 3794 | 95 | 1 | 775 | 107 | 10 |
| γ-butyrolactone | 104 | 104 | 11 | 804 | 100 | 1 | 4318 | 108 | 3 | 802 | 91 | 7 |
| γ-valeroactone | 100 | 100 | 9 | 789 | 99 | 1 | 4310 | 108 | 3 | 861 | 107 | 7 |
| 3-ethylpyridine | 95 | 95 | 9 | 807 | 101 | 8 | 4075 | 102 | 3 | 868 | 112 | 9 |
| Benzaldehyde | 99 | 99 | 2.1 | 794 | 99 | 2 | 4115 | 103 | 6 | 732 | 91 | 6 |
| 5-methylfurfural | 100 | 100 | 6 | 776 | 97 | 1 | 4099 | 102 | 3 | 844 | 108 | 10 |
| Methyl heptenone | 101 | 101 | 5 | 744 | 93 | 6 | 3939 | 98 | 5 | 818 | 95 | 8 |
| Ethyl caproate | 96 | 96 | 1 | 829 | 104 | 2 | 4307 | 108 | 12 | 782 | 89 | 3 |
| 2,3,5-trimethylpyrazine | 94 | 94 | 10 | 784 | 98 | 11 | 3919 | 98 | 9 | 851 | 108 | 5 |
| Cis-3-hexenylacetate | 111 | 111 | 4 | 834 | 104 | 8 | 3365 | 84 | 9 | 730 | 101 | 5 |
| 4-methyl-2-(1-methylethyl)-thiazole | 98 | 98 | 6 | 761 | 95 | 0.3 | 3503 | 88 | 2 | 861 | 101 | 8 |
| 2-acetylpyrazine | 102 | 102 | 10 | 788 | 98 | 1 | 4135 | 103 | 2 | 857 | 103 | 6 |
| Methyl cyclopentenolone | 94 | 94 | 6 | 782 | 98 | 4 | 4267 | 107 | 3 | 785 | 94 | 4 |
| Limonene | 98 | 98 | 10 | 829 | 104 | 0.3 | 4340 | 108 | 4 | 816 | 104 | 1 |
| 2-acetylpyridine | 97 | 97 | 9 | 777 | 93 | 4 | 4423 | 111 | 3 | 873 | 100 | 3 |
| Benzyl alcohol | 103 | 103 | 2 | 818 | 102 | 9 | 4418 | 110 | 2 | 771 | 92 | 1 |
| Melonal | 102 | 102 | 10 | 805 | 101 | 3 | 3890 | 97 | 8 | 761 | 110 | 9 |
| Furaneol | 94 | 94 | 4 | 742 | 93 | 4 | 3945 | 99 | 4 | 871 | 94 | 4 |
| γ-hexalactone | 110 | 110 | 0.2 | 745 | 93 | 2 | 4492 | 112 | 1 | 793 | 97 | 7 |
| Isoamyl butyrate | 91 | 91 | 0.9 | 828 | 104 | 4 | 4205 | 105 | 1 | 856 | 95 | 7 |
| 2-acetylpyrrole | 108 | 108 | 11 | 812 | 102 | 3 | 4383 | 110 | 3 | 783 | 112 | 5 |
| Diethyl malonate | 102 | 102 | 6 | 777 | 97 | 1 | 4250 | 106 | 4 | 758 | 107 | 3 |
| 2,3,5,6-tetramethylpyrazine | 100 | 100 | 2 | 757 | 95 | 2 | 3936 | 98 | 3 | 853 | 95 | 9 |
| Epoxydihydrolinalool (2 isomers) | 105 | 105 | 7 | 795 | 99 | 2 | 4264 | 107 | 4 | 815 | 103 | 4 |
| Ethyl heptanoate | 107 | 107 | 3 | 778 | 97 | 5 | 4063 | 102 | 8 | 848 | 112 | 8 |
| Tetrahydrolinalool | 103 | 103 | 0.3 | 789 | 99 | 3 | 4245 | 106 | 5 | 788 | 107 | 6 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Geranyl propionate | 106 | 106 | 1 | 795 | 99 | 3 | 4202 | 105 | 7 | 763 | 92 | 5 |
| Linalool | 103 | 103 | 6 | 773 | 97 | 2 | 4077 | 102 | 1 | 822 | 112 | 7 |
| Ethyl-3-methylthiopropionate | 101 | 101 | 6 | 785 | 98 | 1 | 4168 | 104 | 0.5 | 764 | 112 | 6 |
| Isopentyl isovalerate | 102 | 102 | 3 | 810 | 101 | 8 | 4074 | 102 | 10 | 771 | 92 | 1 |
| Maltol | 107 | 107 | 12 | 734 | 92 | 0.5 | 4345 | 109 | 3 | 758 | 107 | 3 |
| Phenylethyl alcohol | 94 | 94 | 4 | 853 | 107 | 0.3 | 4217 | 105 | 3 | 866 | 95 | 4 |
| 2-Isopropyl-5-methylhex-2-enal (2 isomers) | 102 | 102 | 3 | 783 | 98 | 3 | 4179 | 104 | 4 | 865 | 101 | 8 |
| Benzyl acetate | 101 | 101 | 6 | 781 | 98 | 2 | 4368 | 109 | 4 | 817 | 111 | 6 |
| Menthone (2 isomers) | 96 | 96 | 6 | 786 | 98 | 3 | 4272 | 107 | 4 | 786 | 88 | 8 |
| Menthol | 110 | 110 | 6 | 802 | 100 | 3 | 4292 | 107 | 4 | 819 | 93 | 2 |
| Diethyl succinate | 108 | 108 | 8 | 794 | 99 | 3 | 4465 | 112 | 3 | 731 | 100 | 10 |
| 4'-methylacetophenone | 103 | 103 | 6 | 791 | 99 | 2 | 4401 | 110 | 2 | 847 | 91 | 9 |
| Styrallyl acetate | 102 | 102 | 6 | 794 | 99 | 2 | 4384 | 110 | 3 | 762 | 91 | 3 |
| α-terpineol (2 isomers) | 101 | 101 | 6 | 810 | 101 | 8 | 4250 | 106 | 4 | 727 | 92 | 10 |
| Methyl salicylate | 104 | 104 | 6 | 790 | 99 | 1 | 4254 | 106 | 1 | 722 | 106 | 2 |
| Ethyl maltol | 103 | 103 | 4 | 748 | 94 | 8 | 4338 | 109 | 2 | 775 | 88 | 8 |
| Decanal | 103 | 103 | 6 | 818 | 102 | 9 | 4500 | 112 | 9 | 860 | 98 | 2 |
| Citronellol | 106 | 106 | 11 | 822 | 103 | 6 | 4384 | 110 | 9 | 738 | 98 | 4 |
| Nerol | 104 | 104 | 3 | 764 | 96 | 8 | 4500 | 113 | 10 | 729 | 112 | 4 |
| Cis-3-Hexenyl valerate | 106 | 106 | 4 | 823 | 103 | 7 | 4154 | 104 | 3 | 845 | 106 | 4 |
| Ethyl phenylacetate | 105 | 105 | 2 | 893 | 112 | 4 | 4454 | 111 | 2 | 842 | 111 | 7 |
| Carvone | 106 | 106 | 6 | 807 | 101 | 2 | 4563 | 110 | 2 | 773 | 111 | 7 |
| Linalyl acetate | 97 | 97 | 5 | 714 | 89 | 2 | 4045 | 101 | 2 | 771 | 97 | 9 |
| Geraniol | 111 | 111 | 2 | 784 | 98 | 2 | 4464 | 112 | 4 | 768 | 110 | 6 |
| Citral | 104 | 104 | 7 | 786 | 98 | 3 | 4450 | 111 | 3 | 788 | 91 | 10 |
| L-menthyl acetate | 101 | 101 | 5 | 813 | 102 | 1 | 4329 | 108 | 5 | 841 | 99 | 7 |
| Theaspirane (2 isomers) | 99 | 99 | 7 | 782 | 98 | 9 | 4181 | 105 | 7 | 775 | 107 | 10 |
| Capric acid** | 878 | 110 | 9 | 1468 | 98 | 6 | 3798 | 97 | 10 | 802 | 91 | 7 |
| Eugenol | 92 | 92 | 6 | 782 | 98 | 4 | 4416 | 110 | 0.7 | 861 | 107 | 7 |
| γ-nonalactone | 105 | 105 | 12 | 800 | 100 | 4 | 4475 | 112 | 1 | 868 | 112 | 9 |
| Hexyl hexanoate | 96 | 96 | 7 | 770 | 96 | 5 | 4443 | 111 | 6 | 732 | 91 | 6 |
| Methyl cinnamate | 102 | 102 | 10 | 778 | 97 | 4 | 4255 | 106 | 1 | 844 | 108 | 10 |
| 3,4-dihydrocoumarin | 93 | 93 | 3 | 793 | 99 | 4 | 4437 | 111 | 1 | 818 | 95 | 8 |
| Vanillin | 107 | 107 | 4 | 748 | 93 | 2 | 4406 | 110 | 1 | 782 | 89 | 3 |
| Anisyl acetate | 103 | 103 | 11 | 783 | 98 | 4 | 4282 | 107 | 2 | 851 | 108 | 5 |
| β-damascone | 99 | 99 | 8 | 770 | 96 | 6 | 4406 | 110 | 2 | 730 | 101 | 5 |
| α-ionone | 102 | 102 | 8 | 782 | 98 | 5 | 4592 | 115 | 6 | 861 | 101 | 8 |
| Ethylvanillin | 99 | 99 | 10 | 741 | 93 | 4 | 4385 | 110 | 0.9 | 857 | 103 | 6 |
| γ-decalactone | 103 | 103 | 6 | 807 | 101 | 5 | 4289 | 107 | 1 | 785 | 94 | 4 |
| Ethyl cinnamate | 102 | 102 | 10 | 782 | 98 | 4 | 4298 | 107 | 0.5 | 816 | 104 | 1 |
| β-ionone | 101 | 101 | 10 | 782 | 98 | 5 | 4355 | 109 | 1 | 873 | 100 | 3 |
| Phenenthyl isovalerate | 100 | 100 | 4 | 802 | 100 | 4 | 4303 | 111 | 1 | 771 | 92 | 1 |
| 5-methyl-2-henyl-2-hexenal (cocal) | 99 | 99 | 11 | 785 | 98 | 5 | 4303 | 108 | 0.4 | 761 | 110 | 9 |
| α,α-dimethylphenethyl butyrate | 100 | 100 | 9 | 784 | 98 | 5 | 3922 | 98 | 3 | 871 | 94 | 4 |
| δ-decalactone | 90 | 90 | 7 | 770 | 96 | 4 | 4322 | 108 | 0.4 | 793 | 97 | 7 |
| Ethyl 3-methyl-3-phenylglycidate | 91 | 91 | 4 | 734 | 92 | 2 | 4041 | 101 | 4 | 856 | 95 | 7 |

| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Raspberry ketone | 97 | 97 | 7 | 729 | 91 | 4 | 4097 | 102 | 1 | 783 | 112 | 5 |
| γ-undecalactone | 99 | 99 | 5 | 795 | 99 | 4 | 4160 | 104 | 1 | 758 | 107 | 3 |
| Hedione (2 isomers) | 93 | 93 | 4 | 778 | 97 | 5 | 4277 | 107 | 0.3 | 853 | 95 | 9 |
| γ-dodecalactone | 93 | 93 | 5 | 775 | 97 | 5 | 4082 | 102 | 0.3 | 815 | 103 | 4 |
| δ-tetradecalactone | 106 | 106 | 9 | 715 | 89 | 4 | 4110 | 103 | 1 | 848 | 112 | 8 |

*For furfuryl alcohol different spiking levels were applied: 300,800 and 4000 ng/mL

** For capric acid different spiking levels were applied: 800,1500 i 4000 ng/mL

**Table S2** Concentrations ( mg/mL ± SD) of determinated flavour chemicals in investigated e – liquid samples. Only detected substances are shown.

| Compound name | Tobacco-flavoured e-liquids | | | | | Apple-flavoured e-liquids | | | | | Cherry-flavoured e-liquids | | | | | Strawberry-flavoured e-liquids | | | | | Menthol-flavoured e-liquids | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Concentration [mg/mL] ± SD (n=3) | | | | | | | | | | | | | | | | | | | | | | | | |
| | Brand | | | | | | | | | | | | | | | | | | | | | | | | |
| | A | B | C | D | E | A | B | C | D | E | A | B | C | D | E | A | B | C | D | E | A | B | C | D | E |
| Ethyl 2-methylpropanoate | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.086 +/- 0.004 | - |
| 1-amylalcohol | - | - | - | - | - | - | - | - | 0.054 +/- 0.002 | - | | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Ethyl butyrate | - | - | - | - | - | - | 0.486 +/- 0.001 | - | - | - | 0.111 +/- 0.006 | 0.224 +/- 0.013 | - | - | (0.013) * | 0.566 +/- 0.008 | 0.23 +/- 0.01 | 7.358 +/- 0.012 | 0.026 +/- 0.001 | 0.73 +/- 0.09 | - | - | - | 0.0130 +/- 0.0007 | - |
| Ethyl lactate | - | - | - | - | - | - | 0.047 +/- 0.002 | - | - | - | - | - | - | - | - | 0.009 +/- 0.001 | - | - | (0.011)* | - | - | - | - | - | - |
| Leaf aldehyde | - | - | - | - | - | 0.06 +/- 0.002 | 0.398 +/- 0.005 | 0.078 +/- 0.003 | 0.093 +/- 0.004 | 0.20+/- 0.02 | - | - | - | - | - | - | - | - | 0.0075 +/- 0.0004 | - | - | - | - | - | - |
| Cis-3-hexenol | - | - | - | - | - | - | 0.166 +/- 0.003 | 0.162 +/- 0.003 | 0.102 +/- 0.002 | - | 0.801 +/- 0.009 | - | - | - | - | 0.49 +/- 0.01 | 0.314 +/- 0.007 | 3.18 +/- 0.05 | 0.219 +/- 0.004 | - | - | - | - | - | - |
| Trans-2-hexenol | - | - | - | - | - | - | 0.216 +/- 0.005 | - | - | - | 0.366 +/- 0.008 | - | - | - | - | 0.050 +/- 0.003 | - | - | - | - | - | - | - | - | - |
| n-Hexanol | - | - | - | - | - | 0.122 +/- 0.008 | 0.153 +/- 0.009 | 0.07 +/- 0.02 | 1.379 +/- 0.007 | 1.6 +/- 0.4 | 0.345 +/- 0.009 | - | - | - | - | 0.045 +/- 0.003 | - | - | - | 0.13 +/- 0.04 | - | - | - | - | 0.025 +/- 0.003 |
| Isopentyl acetate | - | - | - | - | - | 2.33 +/- 0.03 | 0.77 +/- 0.01 | 0.217 +/- 0.007 | 0.156 +/- 0.002 | 1.5 +/- 0.2 | 0.031 +/- 0.003 | - | 0.56 +/- 0.01 | 0.577 +/- 0.01 | - | - | (0.017) * | - | - | - | - | - | - | - | - |
| Furfuryl alcohol | - | - | - | - | - | - | 0.027 +/- 0.002 | 0.0053 +/- 0.0003 | 0.002 3 +/- 0.000 3 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| γ-valeroactone | 0.0129 +/- 0.0005 | - | - | - | - | - | - | - | - | - | 0.0083 +/- 0.0001 | - | - | - | - | 0.0106 +/- 0.0005 | - | - | - | - | 0.0085 +/- 0.0004 | - | - | - | - |
| Benzaldehyde | - | - | - | - | - | - | - | - | - | - | 0.302 +/- 0.009 | 0.228 +/- 0.008 | 0.043 +/- 0.004 | 0.68 +/- 0.01 | 1.30 +/- 0.02 | - | - | - | - | - | - | - | - | - | - |
| 5-methylfurfural | - | - | - | - | - | - | - | - | - | - | 0.0008 3 +/- 0.0000 3 | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Ethyl caproate | - | - | - | - | - | 0.151 +/- 0.004 | - | - | - | - | 0.054 +/- 0.002 | - | 0.093 +/- 0.004 | - | - | 0.116 +/- 0.008 | 0.179 +/- 0.005 | - | 0.171 +/- 0.006 | 0.0083 +/- 0.0008 | - | - | - | - | - |
| 2,3,5-trimethylpyrazine | 0.038 +/- 0.002 | 0.071 +/- 0.003 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cis-3-hexenylacetate | - | - | - | - | - | - | 0.0057 +/- 0.0003 | 0.0093 +/- 0.0003 | 0.139 +/- 0.007 | - | 0.0146 +/- 0.0004 | - | - | - | - | 0.0348 +/- 0.0002 | 0.041 +/- 0.002 | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 2-acetylpyrazine | - | 0.094 +/- 0.003 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Methyl cyclopentenolone | 0.201 +/- 0.006 | - | 0.57 +/- 0.03 | 1.16 +/- 0.02 | - | - | 0.0080 +/- 0.0002 | - | - | - | - | - | 0.160 +/- 0.005 | 0.0081 9 +/- 0.008 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| 2-acetylpyridine | - | - | - | 0.0093 +/- 0.0003 | - | - | - | - | - | - | 0.0051 +/- 0.0001 | 0.34 +/- 0.01 | 0.225 +/- 0.004 | 0.0508 +/- 0.0002 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Benzyl alcohol | - | - | - | - | - | - | 0.0248 +/- 0.0008 | - | - | - | 0.0240 +/- 0.0007 | 1.54 +/- 0.05 | 1.06 +/- 0.02 | 0.244 +/- 0.001 | 0.0142 +/- 0.0007 | 0.018 +/- 0.001 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Furaneol | 0.068 +/- 0.002 | - | - | - | - | - | 0.62 +/- 0.01 | - | - | - | 0.187 +/- 0.005 | 0.011 +/- 0.003 | - | - | - | 1.34 +/- 0.03 | - | 0.440 +/- 0.008 | - | - | - | - | - | - | - | - | - | - | - | - |
| γ-hexalactone | - | - | - | - | - | - | - | - | 0.194 +/- 0.007 | - | - | - | - | - | - | - | - | - | 0.071 +/- 0.001 | - | - | - | - | - | - | - | - | - | - | - |
| Isoamyl butyrate | - | - | - | - | - | - | - | - | 0.225 +/- 0.001 | - | - | - | - | - | - | 0.025 +/- 0.002 | - | - | 0.0842 +/- 0.0004 | - | - | - | - | - | - | - | - | - | - | - |
| 2,3,5,6-tetramethylpyrazine | 0.0052 +/- 0.0002 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Ethyl heptanoate | - | - | - | - | - | - | - | - | - | - | - | 0.0783 +/- 0.0035 | 0.121 +/- 0.006 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Tetrahydrolinalool | - | - | - | - | - | - | - | - | - | - | - | 0.0083 +/- 0.0008 | 0.0138 +/- 0.0003 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Geranyl propionate | - | - | - | - | - | - | - | - | 0.0598 +/- 0.0005 | - | - | - | - | - | - | - | - | 0.0333 +/- 0.0004 | - | - | - | - | - | - | - | - | - | - | - | - |
| Linalool | - | - | - | - | - | - | - | - | - | - | 0.031 +/- 0.002 | - | 0.007 +/- 0.001 | - | - | - | - | 0.69 +/- 0.01 | - | - | 0.0076 +/- 0.0002 | - | - | - | 0.047 +/- 0.006 | | | | | |
| Isopentyl isovalerate | - | - | - | - | - | 0.26 +/- 0.01 | 0.00910 +/- 0.00005 | - | - | 0.49+/- 0.03 | - | - | - | - | - | 0.032 +/- 0.002 | 0.091 +/- 0.001 | 0.0065 +/- 0.0002 | - | - | - | - | - | - | - | - | - | - | - | - |
| Maltol | (0.018)* | (0.017)* | (0.0099)* | - | (0.011)* | (0.0090)* | (0.019)* | - | 1.245 +/- 0.045 | - | 0.0411 +/- 0.0065 | (0.0094)* | - | 0.081 +/- 0.012 | - | (0.013)* | (0.012)* | - | - | - | (0.013)* | (0.011)* | - | 0.0221 +/- 0.0048 | - | | | | | |
| Phenylethyl Alcohol | - | - | - | - | - | - | - | - | - | - | 0.0044 +/- 0.0007 | - | - | - | - | - | - | - | - | - | - | - | - | - | (0.082)* | | | | | |
| 2-Isopropyl-5-methylhex-2-enal (2 isomers) | - | - | - | - | - | - | - | - | 0.09 +/- 0.01 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | | | | | |

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Menthone (2 isomers) | - | - | - | - | - | - | - | - | - | - | - | - | 0.0148 +/- 0.0009 | - | - | - | - | - | - | - | - | - | 1.082 +/- 0.009 | 0.891 +/- 0.006 | 0.560 +/- 0.009 | 2.968 +/- 0.038 | 2.60 +/- 0.07 |
| Benzyl acetate | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.0124 +/- 0.0003 | - | - | - | - | - | - | - | - | - | - | - | 0.0398 +/- 0.0006 | - |
| Menthol | - | - | 0.253 +/- 0.002 | - | - | - | - | 0.62 +/- 0.02 | - | - | - | - | 1.10 +/- 0.02 | - | - | 0.0057 +/- 0.0004 | - | 0.66 +/- 0.03 | - | - | 11.4 +/- 0.3 | 10.8 +/- 0.4 | 12.2 +/- 0.2 | 11.93 +/- 0.09 | 6.19 +/- 0.05 |
| 4`-methylacetophenone | - | - | - | - | - | - | - | - | - | - | - | - | 0.067 +/- 0.001 | - | - | - | - | - | - | - | - | - | - | 0.01619 +/- 0.00009 | - |
| Styrallyl acetate | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.0131 +/- 0.0004 | - | - | - | - | - | - | - | - | - | - |
| α-terpineol (2 isomers) | - | - | - | - | - | - | - | - | - | - | - | 0.133 +/- 0.003 | - | - | - | - | - | - | - | - | 0.017 +/- 0.002 | - | - | 0.034 +/- 0.002 | 0.072 +/- 0.002 |
| Ethyl maltol | 0.43 +/- 0.04 | 0.04 +/- 0.002 | 0.53 +/- 0.01 | 0.45 +/- 0.07 | (0.013) * | 0.024 +/- 0.008 | 0.31 +/- 0.01 | 0.01649 +/- 0.00008 | 0.019 +/- 0.003 | - | 0.19 +/- 0.02 | 0.35 +/- 0.01 | 0.0169 +/- 0.0007 | 0.04 +/- 0.02 | - | 0.26 +/- 0.03 | 0.018 +/- 0.001 | 0.019 +/- 0.003 | 0.33 +/- 0.02 | - | 0.05 +/- 0.02 | 0.022 +/- 0.001 | 0.03 +/- 0.001 | 0.49 +/- 0.01 | - |
| Ethyl 3-methyl-3-phenylglycidate (2 isomers) | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.297 +/- 0.027 | - | - | - | - | - | - | - | - | - | - |
| Citronellol | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.0061 +/- 0.0007 | - | - | - | - | - | - | - | - | - | - | - | - |
| Cis-3-Hexenyl valerate | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.018 +/- 0.001 | 0.027 +/- 0.003 |
| Carvone | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.93 +/- 0.01 | - | - | 0.608 +/- 0.009 | 0.042 +/- 0.001 |
| Linalyl acetate | - | - | - | - | - | - | - | - | - | - | - | - | 0.03715 +/- 0.00008 | - | - | - | - | - | - | - | 0.35 +/- 0.01 | - | - | - | 0.021 +/- 0.003 |
| Geraniol | - | - | - | - | - | - | - | - | - | - | - | - | 0.315 +/- 0.004 | - | - | - | - | - | - | - | - | - | - | - | - |
| L-menthyl acetate | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.160 +/- 0.008 | 0.1928 +/- 0.0007 | 0.132 +/- 0.009 | 1.312 +/- 0.003 | 0.698 +/- 0.038 |
| Capric acid | 0.08 +/- 0.01 | - | - | - | - | - | - | - | - | - | (0.052) * | - | - | - | - | - | - | - | - | - | (0.058) * | - | - | - | - |
| Eugenol | - | - | - | - | - | - | - | - | - | - | - | 0.0098 +/- 0.0002 | 0.00525 +/- 0.00003 | - | 0.136 +/- 0.009 | - | - | - | - | - | | - | - | - | - |
| γ-nonalactone | - | - | - | - | - | - | - | - | 0.00386 +/- 0.000008 | - | - | 0.0079 +/- 0.0001 | - | - | - | - | - | - | - | - | - | - | - | 0.00545 +/- 0.00005 | - |

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Hexyl hexanoate | - | - | - | - | - | - | - | - | - | - | 0.055 +/- 0.002 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Methyl cinammate | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.236 +/- 0.003 | 0.21 +/- 0.02 | - | 0.15758 +/- 0.00005 | - | - | - | - | - | - | - | - | - | - | - | - |
| Vanillin | - | 0.011 +/- 0.002 | - | 0.008 +/- 0.002 | - | 0.014 +/- 0.002 | 0.030 +/- 0.001 | 0.05 +/- 0.03 | 0.033 +/- 0.004 | - | 1.64 +/- 0.04 | 0.098 +/- 0.004 | 1.83 +/- 0.01 | 0.2335 +/- 0.0008 | - | 0.012 +/- 0.001 | - | 2.53 +/- 0.06 | - | - | 0.014 +/- 0.001 | - | - | - | - | - | - | - | - | - | - | - |
| Anisyl acetate | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.029 +/- 0.002 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| β-damascone | - | 0.0351 +/- 0.0005 | - | 0.105 +/- 0.007 | - | - | - | - | - | 0.0144 +/- 0.0007 | - | - | 0.0186 +/- 0.0005 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| α-Ionone | - | - | - | - | - | - | - | - | - | - | - | - | 0.0845 +/- 0.0002 | 0.0312 +/- 0.0009 | 0.0021 +/- 0.0001 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Ethyl Vanillin | - | - | 0.208 +/- 0.003 | - | - | - | - | - | - | - | - | - | 0.907 +/- 0.008 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| γ-decalactone | - | - | - | - | - | - | - | - | - | 0.0076 +/- 0.0009 | - | - | - | - | 0.0051 +/- 0.0002- | 0.181 +/- 0.006 | 0.31 +/- 0.02 | 2.63 +/- 0.04 | 0.2892 +/- 0.0007 | 0.0072 +/- 0.0004 | - | - | - | - | - | - | - | - | - | - | - | - |
| Ethyl cinammate | - | - | - | - | - | - | - | - | - | - | 0.0142 +/- 0.0003 | - | - | - | 0.00077 +/- 0.00002 | 0.176 +/- 0.006 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| β-ionone | - | - | - | - | - | - | - | - | - | - | - | - | 0.160 +/- 0.002 | 0.069 +/- 0.002 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Cocal | - | - | - | - | - | - | - | - | - | - | - | - | 0.0080 +/- 0.0001 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Raspberry ketone | - | - | - | - | - | - | - | - | - | - | 0.0091 +/- 0.0009 | - | 0.0149 +/- 0.0003 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| γ-undecalactone | - | - | - | - | - | 0.12 +/- 0.01 | - | - | - | - | - | 0.037 +/- 0.001 | 0.137 +/- 0.002 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| Hedione (2 isomers) | - | - | - | - | - | - | - | - | - | - | - | - | - | - | 0.00042 +/- 0.00008 | - | - | - | 0.0618 +/- 0.0002 | 0.00036 +/- 0.00008 | - | - | - | - | - | - | - | - | - | - | - | - |

*Underlined compounds are indicated on the label*

* *value $C_{min}$ <x<LOQ*