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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.

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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*

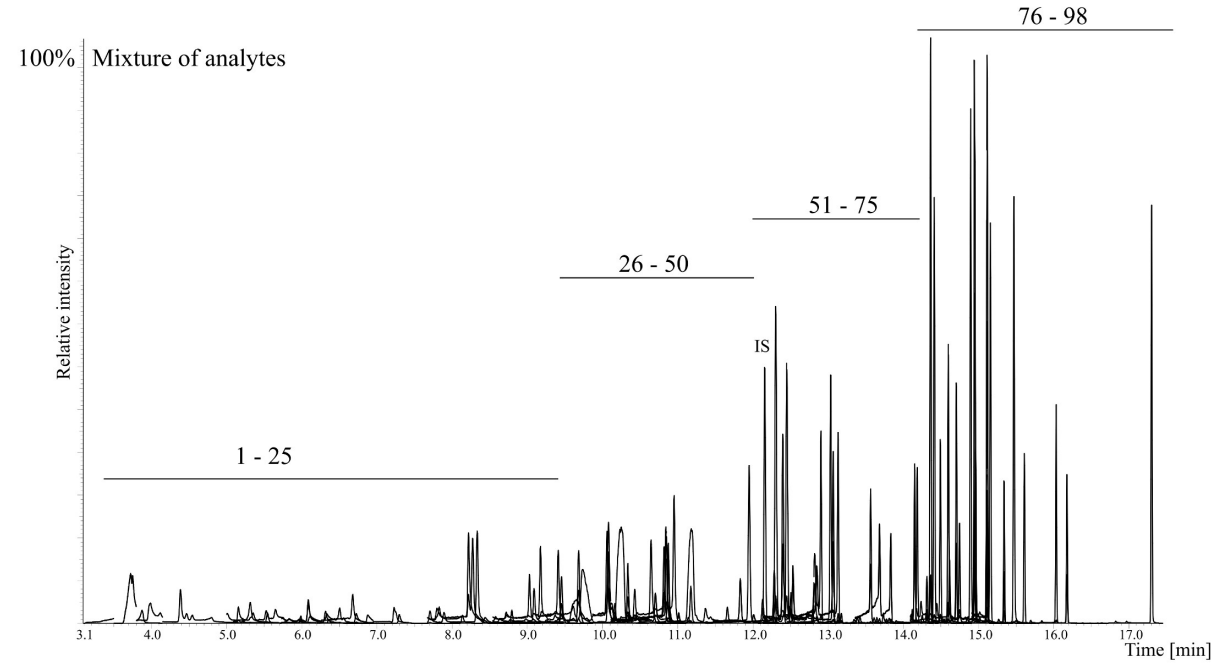
Figure 5. *Scatter plot showing the distribution levels of common compounds within given flavours*

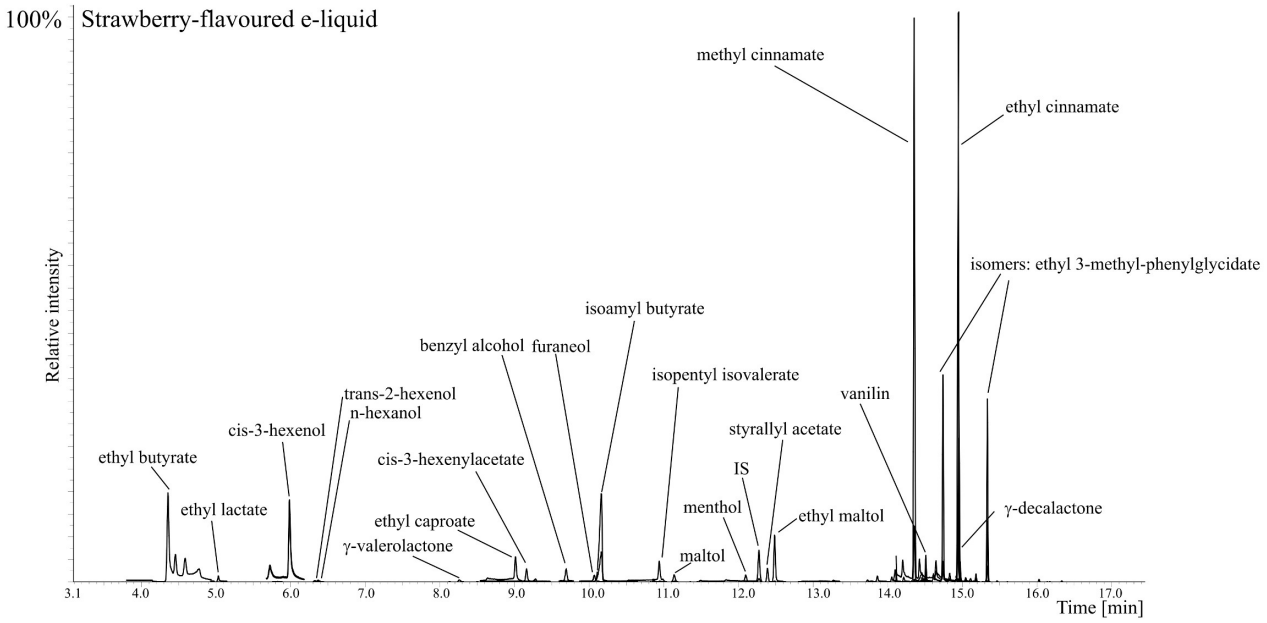
List of supplementary material:

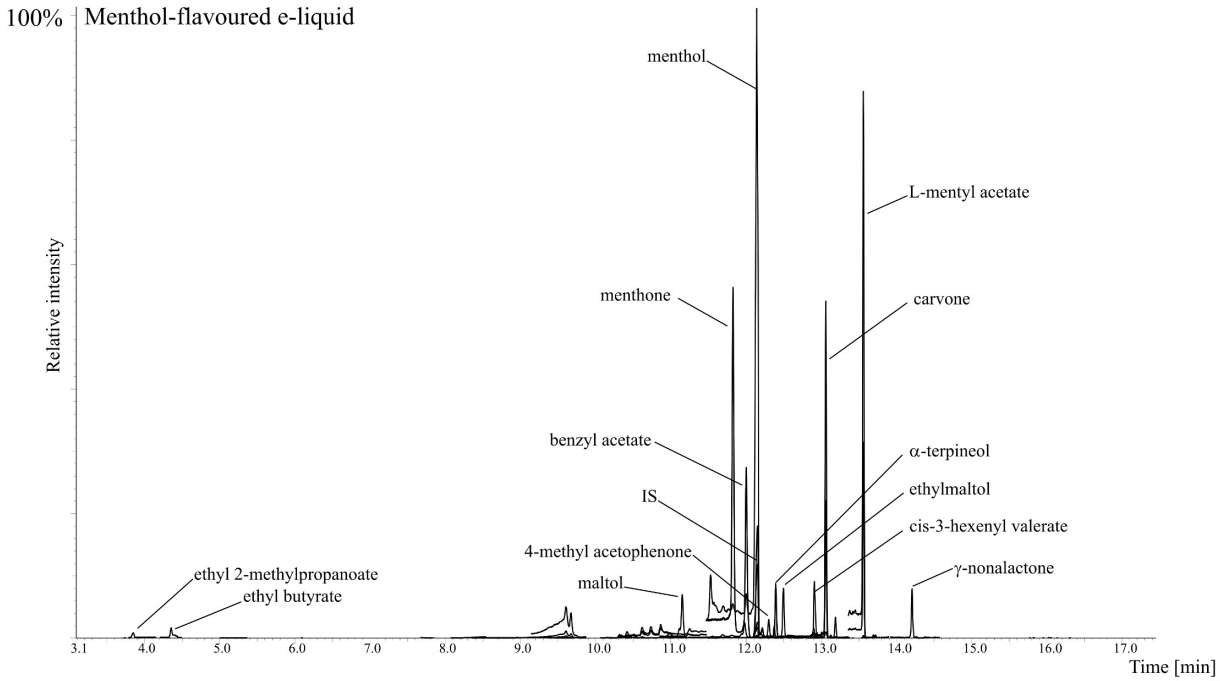
Table S1. *Repeatability and precision data of developed method*

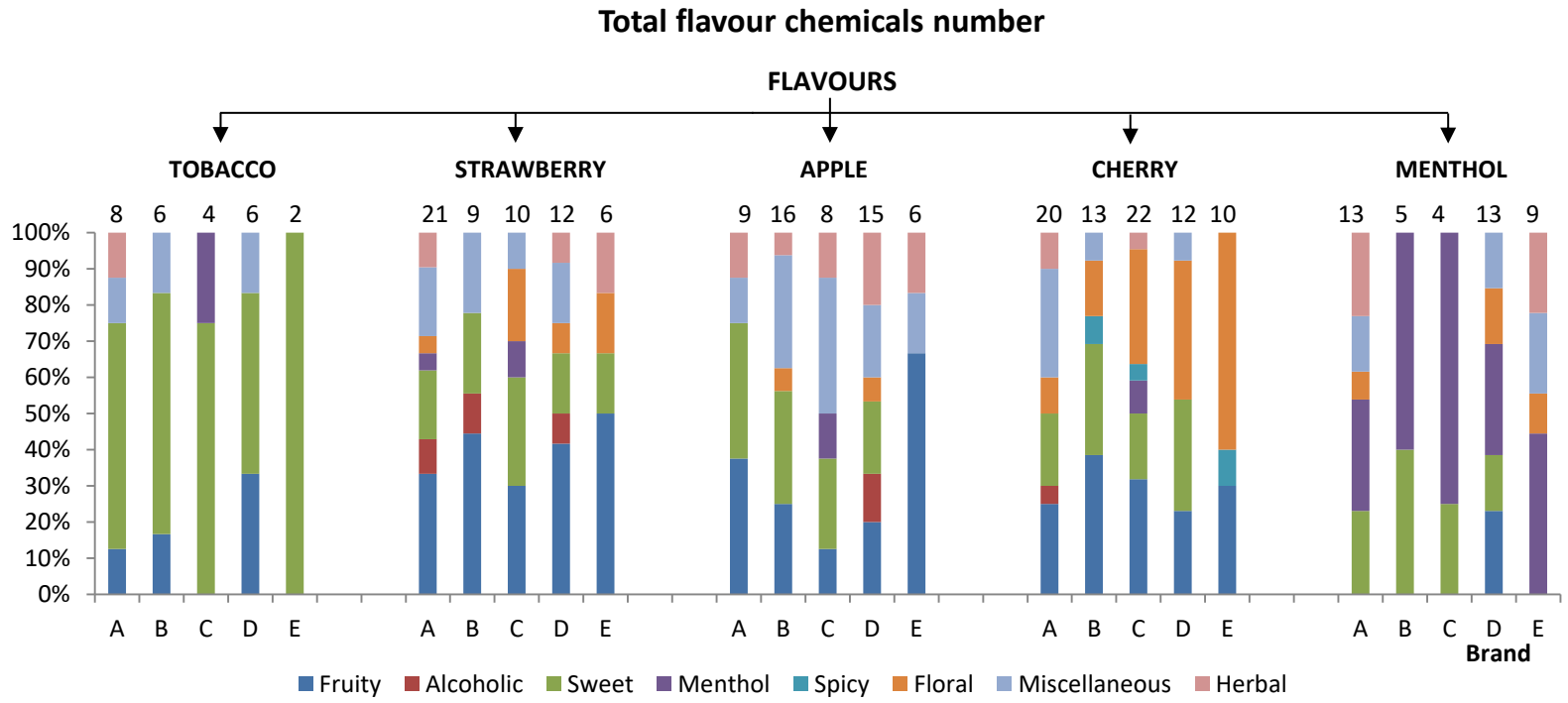
Table S2. *Concentrations (mg/mL ± SD) of determinated flavour chemicals in investigated e – liquid samples*

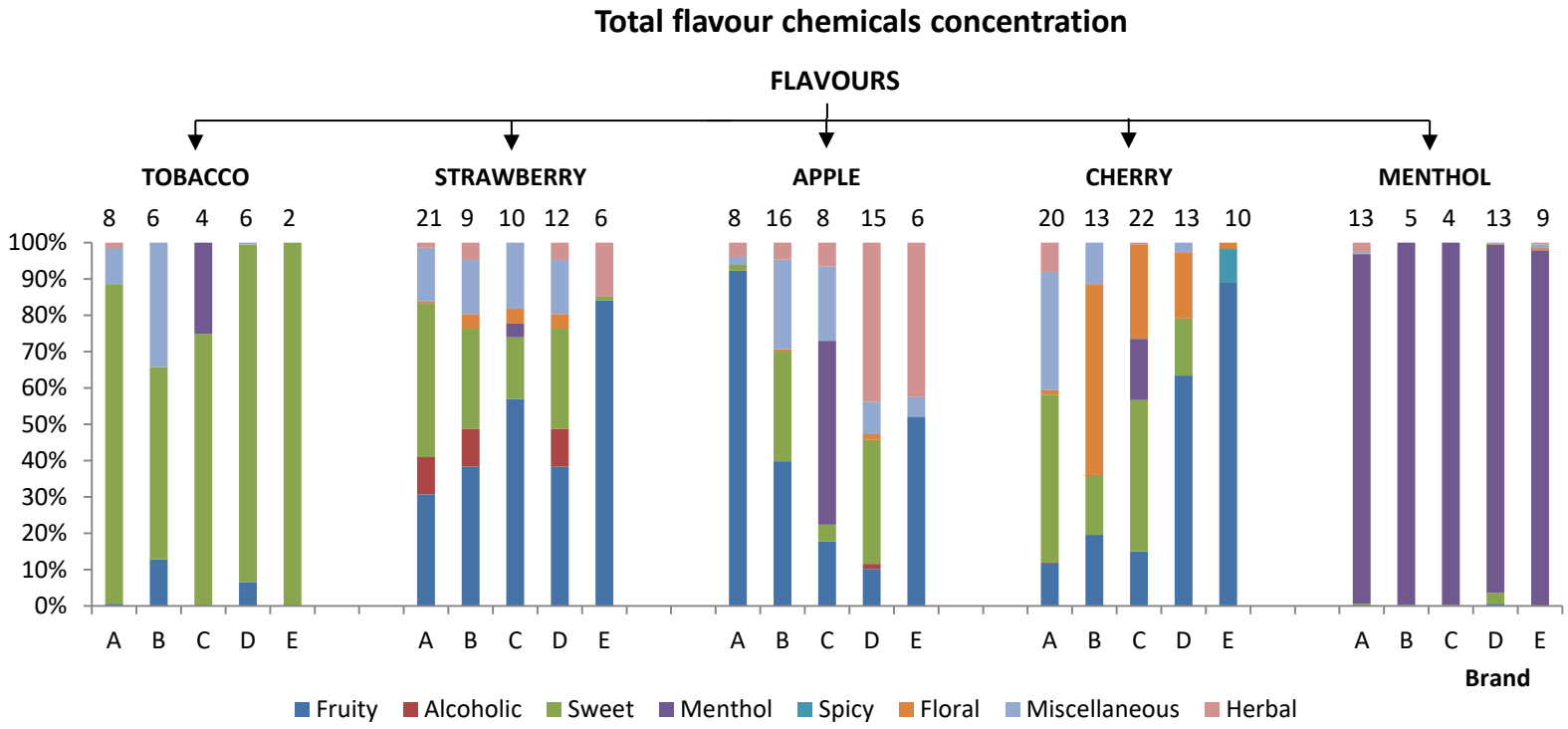
Figure S1. *Comparison of total flavour concentration and price among investigated brand and flavours. Prices are given for bottle of e-liquid of volume 10 mL.*


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]

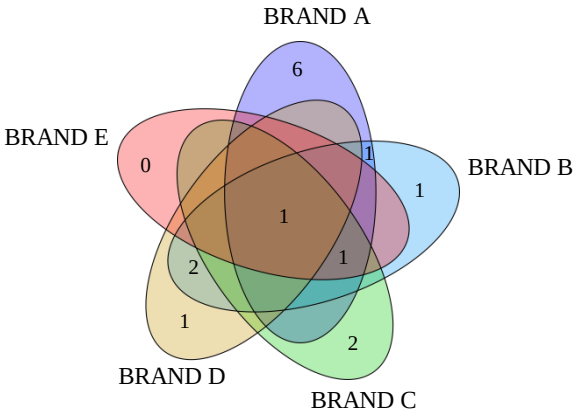

100%
Strawberry-flavoured e-liquid
Relative intensity
methyl cinnamate
ethyl cinnamate
isomers: ethyl 3-methyl-phenylglycidate
isoamyl butyrate
benzyl alcohol
furaneol
isopentyl isovalerate
vanilin
trans-2-hexenol
n-hexanol
cis-3-hexenol
styrallyl acetate
ethyl butyrate
cis-3-hexenylacetate
IS
menthol
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]

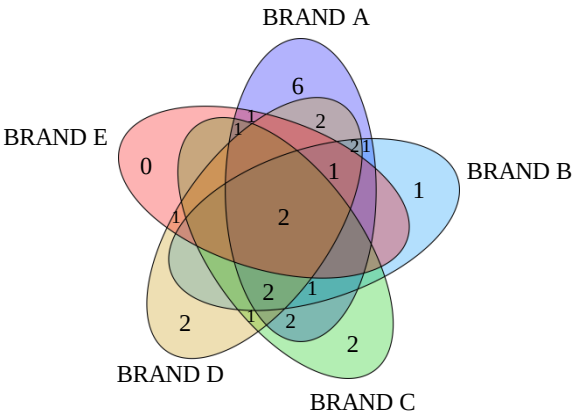




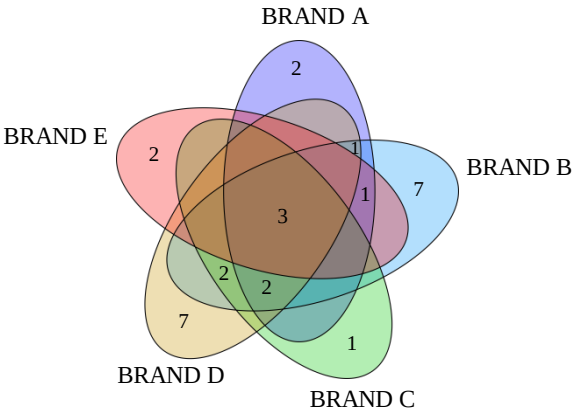
TOBACCO



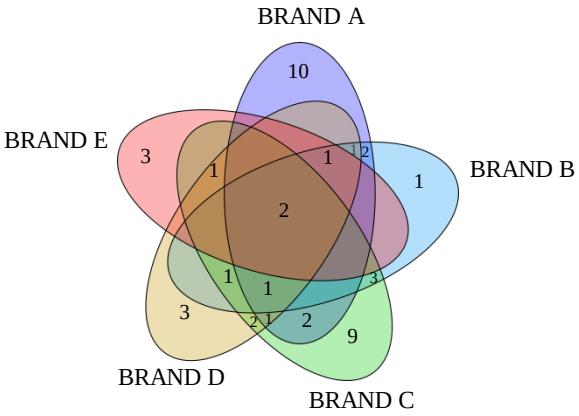
STRAWBERRY



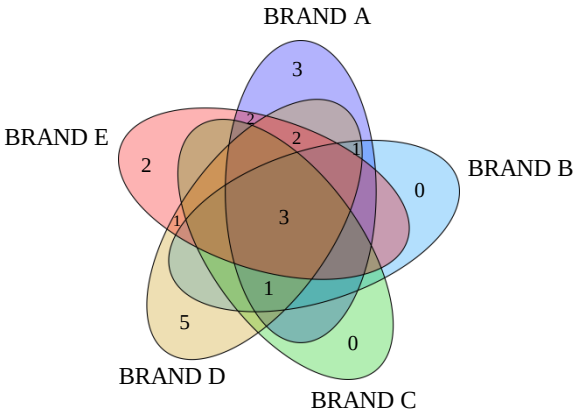
APPLE



CHERRY

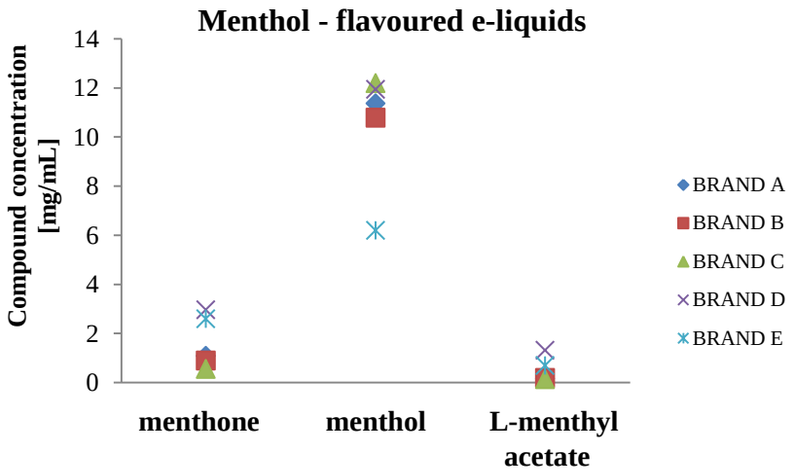


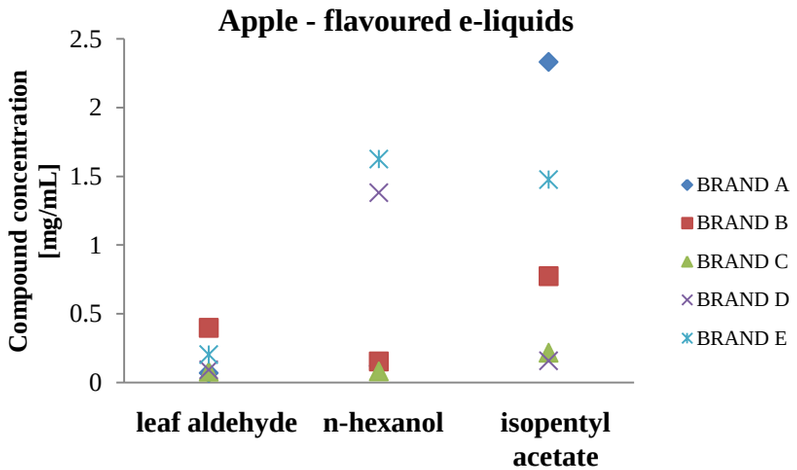
MENTHOL

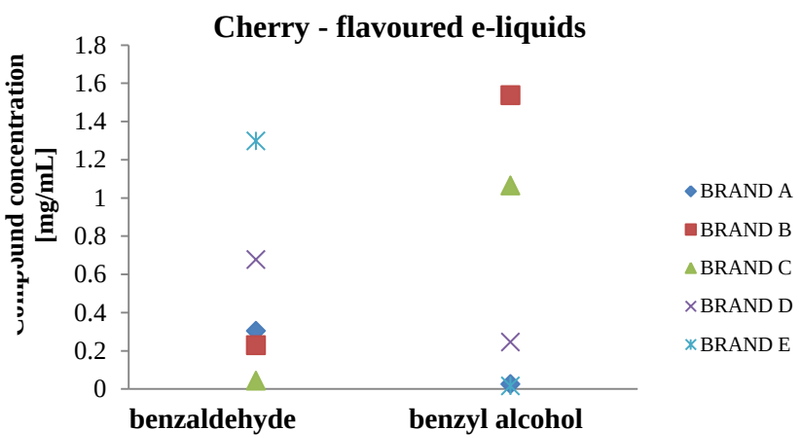


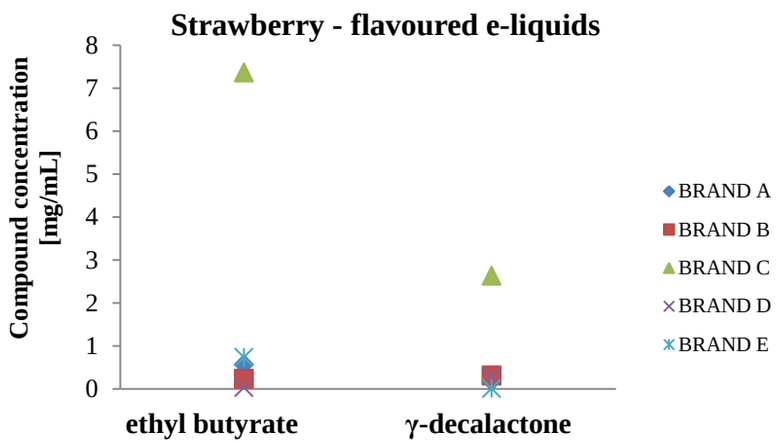
Legend

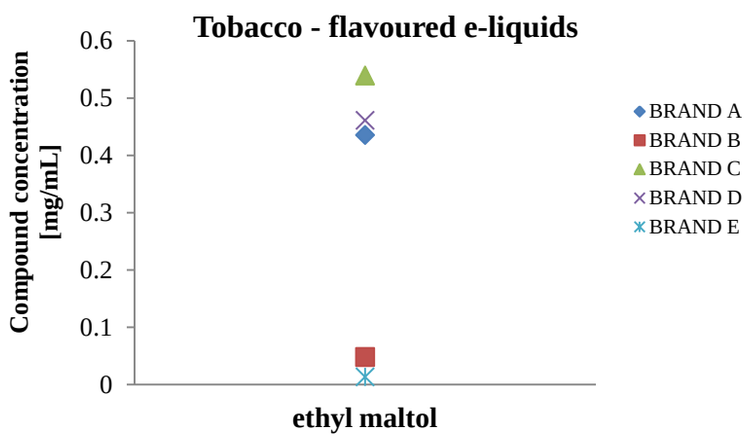
Flavour	Common flavour chemicals (for 100% samples)	Common flavour chemicals (for 80 % samples)
TOBACCO	Ethyl maltol	-
STRAWBERRY	Ethyl butyrate, γ – decalactone	cis-3-hexenol, Ethyl maltol Ethyl caproate
APPLE	Leaf aldehyde, N-hexanol, Isopentyl acetate	Ethyl maltol, Vanillin
CHERRY	Benzaldehyde, Benzyl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











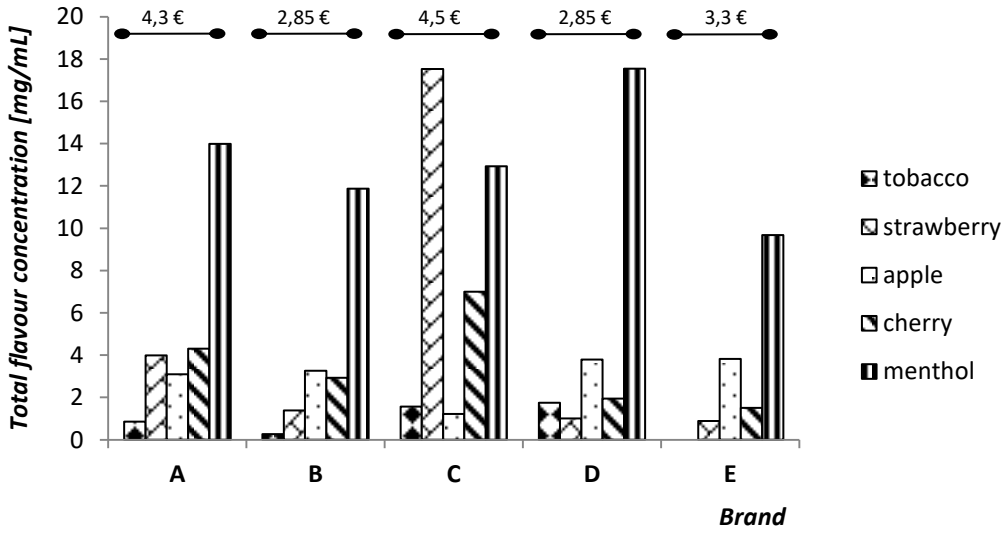


Table S1 *Repeatability and precision data of developed method*

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*