Quick insights into whisky – investigating rapid and efficient methods for sensory evaluation and chemical analysis

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Quick insights into whisky – investigating rapid and efficient methods for sensory evaluation and chemical analysis

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Abstract

The evaluation of aroma properties of beverages both analytically as well as with human sensory is a challenging task and most often related to time- and cost-intensive analyses. Whisky is a spirit offering a wide variety of aroma impressions caused by a complex mixture of aroma active compounds. In the present study, methods for the efficient evaluation of aroma characteristics are evaluated for 16 whisky samples of different origins (Scotch and American). Rate all that apply (RATA) was applied as a rapid sensory method for the sensory evaluation of whiskies. Sensory evaluation of the samples led to the determination of eight significant aroma attributes: Caramel / cream caramel / toffee, vanilla, (canned) peach, phenolic, smoky, fruity, flowery and (fermented) apple / cider. Chemical analysis was conducted by stir bar sorptive extraction (SBSE) coupled to gas chromatography mass spectrometry in combination with an in-house data processing tool for automated analyte detection. Through chemical analysis of the whisky samples and automated compound detection, over 200 mostly aroma-active volatiles were reported. To test both approaches for their potential for sample classification, a simple classification problem (Scotch vs. American) was applied. Linear discriminant analysis (LDA) indicates both that sensory evaluation by RATA (97.86%) and the applied analytical procedure (96.94%) are suitable for the distinction between the two whisky types. For both approaches, markers were identified for the classification. These investigations build a solid foundation for the implementation of a versatile platform for rapid and efficient aroma evaluation for various foodstuffs and beverages.

Keywords (4-6)

Whisky, gas chromatography mass spectrometry, automated compound detection, human sensory, classification

Introduction

Whisky is a complex spirit offering a large variety of sensory experiences. Therefore, it is highly appreciated and popular amongst casual consumers and connoisseurs equally. The sensory characteristics of the beverage offer a huge spectrum, ranging from floral, fruity to phenolic and smoky notes [1, 2]. Many studies have so far focused on the characterization of whisky constituents, including aroma compounds [3–6]. Aroma active volatiles that have often been reported to be found in different kinds of Whiskies include for example 2-phenylethanol, 3-methylbutylacetate, furfural, *cis / trans* whisky lactone, vanillin, γ-nonalactone as well as different phenolic compounds such as 4-ethylphenol and 4-methylphenol. Beyond that, carbonic acids such as octanoic and decanoic acid as well as different ethyl and isoamyl esters represent typical whisky compounds [4, 5, 7–10]. The aroma profile of whisky perceived through smelling or drinking of the spirit results from a wide range of compounds in different concentrations and of different odor qualities [2, 4, 5]. As a whisky's aroma is the most important feature of the beverage when it comes to consumer preference, the monitoring and maintaining of high sensory quality standards are crucial. Aroma analysis is a complex and versatile procedure that, depending on the scope of the analysis, includes various different steps. Generally, gas chromatography coupled to mass spectrometry (GC-MS) and/or an olfactory detection port (OPD) as GC-MS/O or GC-O plays a major role for the analysis of volatile aroma compounds. To identify these compounds, mainly three factors are taken into account: the mass spectra, the (linear) retention indices (RI) as well as the odor quality detected at the ODP [5, 11, 12]. The comparison with reference compounds then leads to unequivocal identification of the aroma compounds. Furthermore, the sampling or sample preparation has to be considered as well. Depending on the

sample matrix, the analytes within the sample as well as the aim of the investigation, different sampling procedures can be applied. For whisky, as for other matrices, these methods vary regarding the time and personnel required, the analytes that are extracted as well as the usage of equipment and solvent [5, 7, 8]. Therefore, the sampling method has to be chosen carefully considering these aspects. There exist various methods for the sample preparation and isolation of volatiles, including aroma-active compounds, from different matrices [8, 13–16]. Relating to aroma compounds' analysis in whisky, different methods for sample preparation and analyte extraction have been applied so far. This includes for example solvent extraction followed by the solvent-assisted flavour evaporation (SAFE) technique [5], (headspace) SPME [6–8] as well as stir bar sorptive extraction (SBSE) [8, 17, 18]. SBSE uses a sorbent-coated stir bar which is placed into the liquid sample [19]. Analyte extraction is based on the partitioning between the sample and the sorbent. For the use of Polydimethylsiloxane (PDMS) as a mostly unpolar sorbent, Baltussen et al [19] proposed the following approximation (eq. 1) to estimate the partitioning of analytes between PDMS and water via its proportionality to the molecule's octanol-water partitioning coefficient ($K_{O/W}$), which is widely available for various different compounds [19].

Eq. 1. $$K_{\frac{PDMS}{W}} = \frac{c_{PDMS}}{c_W} = \frac{m_{PDMS}}{m_W} \times \frac{V_W}{V_{PDMS}} \approx K_{\frac{O}{W}}$$

In eq. 1 $K_{O/W}$ and $K_{PDMS/W}$ are the octanol/water and PDMS/water partitioning coefficients, respectively; c_{PDMS} and c_w are the analyte concentrations in the PDMS and water phase; m_{PDMS} and m_W are the analyte masses in PDMS and water; V_{PDMS} and V_w represent the PDMS and water phase volumes.

A thorough investigation to reliably determine the full spectrum of aroma compounds or the determination of key aroma compounds including quantitative methods, requires GC-MS/O or even 2-dimensional GC-MS/O coupled to effortful analyte extraction methods [5, 6, 11, 20]. However, there is a need for fast or more efficient methods for some applications that require a reliable overview and high quality results on the aroma compounds present in the sample while time and cost are the limiting factor. The same applies for sensory analysis, where the need for rapid sensory methods has risen and respective methods have been explored [2, 21–23]. Additionally, the data obtained might be used to solve classification problems, such as the differentiation between sample types, e.g. differing in origin or ingredients.

Subsequent to the analytical procedure, data analysis of the generated gas chromatographic data requires expertise and time. The combination of (fast) analytical or detection methods and chemometrics for the evaluation or classification of products, such as foods, is a very promising approach and has been investigated for different applications. Zhang et al. [24] used an electronic nose in combination with data science methods for the classification of Blended and Single Malt Scotch whiskies. Using six samples of different brands, regions and style (three blended Scotch and three single malt Scotch Whiskies), they achieved classification accuracies of 96.15%, 100 % and 92.31 % respectively during a field test with 58 datasets [24]. Different pattern recognition procedures based on GC-MS data for the classification of Scotch, Irish and Bourbon whisky were tested by González-Arjona et al. [25]. Best results were obtained by the use of artificial neural networks (ANN). Zhu et al. [26] investigated the volatile constituents of Sauvignon Blanc wines and applied prediction models for the correlation of analytical and sensory data. Following sample analysis by means of ultra-fast GC coupled to

an electronic nose, Liu et al. [27] investigated the clustering of different types of vinegar by applying PCA and orthogonal partial least square discriminant analysis (OPLS-DA).
Beyond that, there are various other fields of application and approaches for the prediction of sample properties or their classification with the use of statistical or machine learning methods based on the chemical sample composition, analytical or sensor data or even optical measurements [28–34].

The field of smart odor analysis, incorporating efficient or fast analytical methods as well as data science, therefore offers promising tools and opportunities not only for efficient aroma analysis but also to gain further insights into large data sets. For this reason we are working on efficient odorant analysis methods for the evaluation of aroma profiles and sensory features for applications where such procedures are applicable and required. For this purpose, we have applied and tested a fast and easily applicable analytical procedure to determine (aroma-active) volatile compounds in whisky using an automated process for the compound detection in the whisky samples [35–37]. Furthermore, aroma characteristics of the samples were investigated by orthonasal sensory analysis applying a rapid sensory method. The analysis of the whisky samples is based on the SBSE method [19] followed by GC-MS analysis. For the data analysis, an in-house, user-friendly compound detection platform [35–37] based on MS and RI data was used. It allows us to generate customized analysis reports for further data analysis. The combination of SBSE, GC-MS and automated processing was used on two model whiskies respectively containing 26 and 27 typical whisky compounds in an ethanol-water ($EtOH/H_2O$) matrix. Results show that the majority of analytes were correctly assigned. Analysis of 16 different whiskies showed up to 153 proposed molecules in the single samples, among those were several volatiles that have previously been reported for whisky. Regarding the sensory analysis of the samples, we used the Rate All That Apply (RATA) [21, 38] method to evaluate the sensory characteristics of the whisky samples by orthonasal evaluation. For both data sets, a linear discriminant analysis (LDA) was applied for the classification of whisky types (Scotch vs. American), achieving up to 97.86 % correct classifications within 5000 random subsets for the sensory data. Direct comparison shows that sensory RATA data and GC-MS data including automated analyte detection were comparably suitable for the classification of the whisky samples (Scotch vs. American). Despite this performance, other analytical procedures should be tested and optimized to evaluate, how analytical data can be used further as an effective and efficient tool to get insights into aroma profiles and facilitate aroma analysis. Taken together, first promising steps for the establishment of a platform for rapid and efficient evaluation and characterization of aroma profiles based on analytical data were made.

Materials and Methods

Samples

For the sensory as well as chemical analysis 16 different commercially available whiskies were selected. These included 9 Scotch and 7 American whiskies of different types and origins (table S2). For dilution of the whisky we used a mineral drinking water (Acqua Panna, Nestlé Deutschland AG, Frankfurt, Germany).

For a standardized evaluation of the whisky samples within chemical and sensory analysis, they have been adjusted to an alcohol content (alcohol by volume, ABV) of 40 % vol. For this purpose, samples with higher alcohol contents than 40 % were diluted by adding the respective amount of drinking water to obtain a total of 170 ml using an Eppendorf pipette and measuring cylinder. For the sensory trials, all samples have additionally

been diluted to an alcohol content of 20 % vol. to gain further insights into the aroma profiles of the samples. Thereby, a certain amount of whisky was filled up with drinking water to a total of 150 ml to obtain the respective ABV percentage of 20 % vol. The respective samples are listed in table S2 in the supplementary material (table S2).

10 mL of each sample were transferred into 40 mL amber glass bottles with screw cap and stored at room temperature for at least 24 h prior to sensory or chemical analysis to ensure comparability between samples and analyses. For the chemical analysis, whisky samples with 40 % ABV were considered, while for the sensory evaluation all samples at 20 %, 40 % or original (if not 40 %) alcohol content were taken into account.

Chemicals and Standards

For the determination of RI values after van den Dool and Kratz [39], a homologous series of n-alkanes C_6-C_{26} (Sigma Aldrich, Steinheim, Germany) was used. For the validation of the sampling procedure as well as the data analysis, two whisky-mimicking solutions (model whiskies) were prepared. The analytes were selected to represent a wide variety of compounds typically found in different kinds of whisky as reported in the literature [2, 4–6, 8, 9] as well as based on preliminary studies [36]. Therefore, the model whiskies contained typical whisky aroma compounds, covering a wide range of chemical functional groups and concentrations. Ethanolic solutions of reference compounds (table S1 for details on suppliers) were prepared. Defined volumes were mixed and filled up to 100 mL ethanol, 2 mL of the ethanolic solution was then filled up with demineralized water to a total of 5 mL to obtain an alcohol content of 40 % vol. For model whisky 1 and 2 the analytes presented in table 1 were used., resulting in 27 single components in whisky model 1 and 26 single whisky components in model 2 (*cis* and *trans* whisky lactone counted as two).

Table 1 concentration of aroma compounds in model whiskies 1 and 2.

Compound	**CAS no.**	**Concentration model whisky 1 [µg / mL]**	**Concentration model whisky 2 [µg / mL]**
β-Damascenone	23696-85-7	0.07	-
Furfural	98-01-1	3.07	1.53
3-Methylbutanal	590-86-3	0.36	0.68
2-Methylbutanal	96-17-3	0.23	0.09
2-Phenylethanol	60-12-8	13.90	8.90
2-Methyl-1-butanol	137-32-6	0.82	-
3-Methyl-1-butanol	123-51-3	9.39	46.93
Isoamyl acetate	123-92-2	2.42	0.72
Phenylethyl acetate	103-45-7	2.47	4.02
Isoamyl octanoate	2035-99-6	0.80	0.16
Isoamyl decanoate	2306-91-4	-	0.31
Ethyl butanoate	105-54-4	0.30	0.30
Ethyl hexanoate	123-66-0	3.65	1.30
Ethyl heptanoate	106-30-9	0.39	-
Ethyl octanoate	106-32-1	3.23	2.02
Ethyl decanoate	110-38-3	2.12	2.76
Ethyl nonanoate	123-29-5	0.20	0.59
Ethyl myristate	124-06-1	0.13	0.21
Ethyl hexadecanoate	628-97-7	0.23	-

Octanoic acid	124-07-2	0.33	0.21
Decanoic acid	334-48-5	0.38	0.38
Dodecanoic acid	143-07-7	-	0.16
cis/trans Whisky-lactone[1]	39212-23-2	0.36	0.36
γ-Nonalactone	104-61-0	0.30	0.35
2-Methoxyphenol	90-05-1	3.36	0.54
Phenol	108-95-2	-	0.12
4-Methylphenol	106-44-5	0.03	0.05
4-Ethylphenol	123-07-9	0.02	-
4-Allyl-2-methoxyphenol (eugenol)	97-53-0	-	0.62
4-Hydroxy-3-methoxy-benzaldehyde (vanillin)	121-33-5	0.36	1.43

[1]counted as two compounds (*cis* and *trans* whisky lactone) separately, resulting in a total of 27 and 26 compounds for whisky model 1 and 2, respectively

Two internal standards were used for the comparison between samples and for the validation of the detection tool. 4-chloro-2-methoxyphenol and undecane were mixed together in an ethanolic solution to obtain concentrations of 40-50 µg/mL (48.2 µg/mL and 43.25 µg/mL, respectively).

Sensory analysis of the samples

For the orthonasal sensory analysis the, the RATA method [21, 38] was used. For this purpose, applicable sensory attributes were selected by trained members of the IVV sensory panel beforehand by reference to single whisky samples: solvent-like (nail polish-like), apple-like (including fermented apple / Cider), pear-like, flowery, butter-like / butter-rum aroma, fruity, woody (freshly cut wood), honey-like, honeydew melon-like, caramel-like / cream caramel-like / toffee-like, peach-like (canned peach), coconut-like, spicy / clove-like, orange-like, smoky, phenolic, vanilla and other. All 16 whisky samples were considered with alcohol contents of 20 and 40 % vol. as well as their original alcohol content (if not at 40 % vol.) resulting in a total of 40 samples. The sensory evaluation was performed by 11 volunteers (members of Fraunhofer IVV sensory panel; 8 female, 3 male, aged 26 to 43) at Fraunhofer IVV. Applying the RATA method, the whisky samples were evaluated within four sessions with 10 whisky samples each. The samples were coded with three-digit numbers and were served to the panellists in a randomized order. To ensure comparable procedure of the sensory evaluation, the panellists were instructed to transfer the 10 mL samples into tasting glasses and instantly close them with loose lids. The sensory evaluation was started after 10 minutes by smelling the sample first and indicating the most applicable attributes (max. 5) followed by an intensity rating for the selected attributes on a monadic scale of 1 (low intensity) to 3 (high intensity). Apart from the given attributes, the participants could also select “other” and qualitatively name further attributes (without intensity scaling) to indicate the appearance of attributes other than the ones listed. For the collection of sensory data, the Software program RedJade (RedJade Software Solutions LLC, Silicon Valley, US) was used.

Sample preparation and analysis via gas chromatography – mass spectrometry

For the chemical analysis, all 16 whisky samples stored in 10 mL aliquots at 40 % vol. alcohol content were considered. For the SBSE, 1 mL of each whisky sample or model whisky (40 % vol.) was spiked with 100 µL of internal standard solution (undecane and 4-chloro-2-methoxyphenol), filled up to 10 mL with demineralized water and 1,0 g of sodium chloride was added. The flask was shaken gently and when all salt was dissolved,

2 mL of the sample were taken and transferred to a 10 mL glass vial with screw lid. A conditioned PDMS-coated Twister® with 1 cm length and 0.5 mm coating thickness (Gerstel GmbH & Co. KG, Mühlheim a. d. Ruhr, Germany) was added. Analytes were extracted subsequently by stirring with the Twister® for 1.5 hours. After extraction, the Twisters® were dried with a lint-free tissue and stored in a closed GC-vial until analysis. For the two model whiskies, two blanks were analyzed by mixing 10 mL of distilled water each with 1 g of sodium chloride. 2 mL were then each stirred with a Twister®. The same was done for the whisky samples, however, only two representative blank Twisters® were analyzed for all 16 whisky samples.

The Twisters® were transferred to thermal desorption (TD) glass tubes for analysis via GC-MS. A TD-Unit (TDU; Gerstel GmbH & Co. KG, Mühlheim a. d. Ruhr, Germany) was used for thermal desorption of the analytes from the Twisters®. The initial temperature was set to 40°C with a solvent vent for 0.5 minutes, then raised to 280 °C at 120°C/min, the final temperature was held for 8 minutes. The helium flow over the TDU was adjusted to 50 mL/min. Following the TD, the analytes were cryo-focused in a cooled injection system (CIS, Gerstel GmbH & Co. KG, Mühlheim a. d. Ruhr, Germany) at -70 °C with liquid nitrogen. Desorption from the CIS was achieved by raising the temperature to 280°C at 12°C/s. The chromatographic separation within the GC (Trace GC Ultra, Thermo Fisher Scientific GmbH, Dreieich, Germany) took place on a DB-FFAP column (30 m x 0,25 mm, film thickness 0,25 µm; J & W Scientific, Agilent Technologies, Waldbronn, Germany). The initial GC oven temperature was held at 40°C for 2 minutes, then raised to 235°C at 8°C/minute and held for 5 minutes. The analytes were transferred to the MS (DSQ II, Thermo Fisher Scientific GmbH, Dreieich, Germany) and detected with electron ionization (EI) at 70 eV in full scan mode (m/z 35 – 399) with MS detection starting after 1 minute.

For the analysis of the *n*-alkane reference [39], a solution of C_6 to C_{26} in pentane (Th. Geyer, Renningen, Germany) was transferred into a micro vial within a TD tube and thermally desorbed (40°C to 280°C at 120°C/min, holding time 5 minutes) and cryo focused (-50°C). Concurrent with the Twister® analysis, the helium flow over the TDU was set to 50 mL/min and the focussing trap was heated to 280°C (12°C/s) to transfer the analytes into the GC-MS system. The same chromatographic settings were applied as in the sample analysis.

Development and optimization of an automated process

For the automated processing of the GC-MS data obtained by the whisky analysis, an in-house developed processing tool was used which we developed previously as described in [35, 37] and in the following section. The tool basically comprises two main steps: (i) raw data processing (ii) compound detection including compound identity proposition.

Raw data processing

The processing of the raw GC-MS data includes the alkane as well as the sample analysis data. For this purpose, a pre-processing pipeline for the examination of GC-MS data in .cdf format was developed by us as described in [35–37] and in the following section. This includes the extraction of intensity matrices as number of scans × m/z area followed by a peak deconvolution as applied by [40] for the alkane as well as sample data. For the processing of the alkane data, a procedure for alkane-peak detection was developed in [37]. Based on this, the alkane chromatograms were analyzed to calculate the RIs (eq. 3) of the compounds found in the sample data. After peak extraction and deconvolution, the sample data underwent a noise reduction step. For this purpose, a

sliding window is used for the estimation and subtraction of noise in each window. This was achieved as described elsewhere [37] by determining the median absolute deviation for each window and its comparison to a threshold value. This allows for the differentiation between signal and noise as well as the determination of outliers. For each peak extracted following this procedure, the respective retention time is recognized and used to determine the RIs together with the retention times of the respective alkane chromatogram. For this purpose, eq. 3 is applied based on the equation by van den Dool and Kratz [39].

Eq. 3 $$RI_x = 100 \times (n + \frac{T_x - T_n}{T_{n+1} - T_n})$$

In Eq. 3, x is the compound for which the linear retention index RI_x is to be calculated, n is the number of C atoms in the alkane occurring at retention time T_n before retention time T_x of compound x, and T_{n+1} is the retention time of the alkane occurring after T_x.

We implemented an algorithm capable of reliably detecting alkanes, compensating for impurities and missing alkane peaks. For this, we made use of the linearly decreasing nature of time intervals between consecutive alkanes [41]. For this purpose, thirteen alkane samples were used, and the difference of distances between consecutive alkanes present in each sample were calculated. A plot of the delta values, i.e., adjacent retention time differences vs retention time between consecutive alkanes in each sample is shown in the supplementary material (fig. S1). This shows a linear decay in the distances between alkanes with time. Using SciPy [42] , a linear model was created with negative slope and positive intercept. Using this concept, an upper and lower threshold were set for deciding how 'far' or 'close' a given peak could be as per the linear model before being marked as 'missing peak' or 'impurity peak'. An alkane peak found during analysis was compared to these thresholds and peaks with retention times greater than the upper threshold were marked as 'missed', i.e., those which had an adjacent alkane peak missing. The location and amplitude of the missing peak was interpolated. Similarly, alkane peaks with retention times less than the lower threshold were marked as redundant and removed.

Since retention index calculations requires two adjacent peaks [39, 41], retention indices could not be calculated for those substances that had an analyte peak detected before the first alkane and after the last alkane since in both cases, there would be no lower and upper bounds respectively to calculate the RI values as per Eq. 1. Thus, to generate retention indices of analyte peaks beyond the range of the alkane, the same model was used to estimate the location of alkane peaks before the first alkane occurrence and after the last alkane occurrence. This information was then used to find the retention indices of analyte peaks using Eq. 1.

General procedure for analyte detection

The raw data processing leads to the extraction of mass spectra and the determination of RIs for every peak detected in the chromatogram. Therefore, the second step aims at proposing analyte identities for the extracted peaks by comparison of mass spectra and RIs with appropriate databases. For this purpose an internal database built with the AMDIS software (National Institute of Standards and Technology, NIST, Gaithersburg, USA) including mass spectra and RI was used. The database comprises around 700 mostly odor-active compounds with MS and RI characteristics and is constantly extended to ensure the covering of relevant whisky compounds. Apart from (aroma-active) volatile compounds typically found in whisky and other foodstuffs, the data base also

contains entries for compounds that do not naturally occur in foods or can predominantly be found in non-food samples. As previously described [35, 37], the comparison of mass spectra was achieved by calculating the cosine similarity [43] between the unknown mass spectrum of the analyte peak and the database mass spectra (eq. 3).

Eq. 4 $$score_{MS} = \frac{\sum_{i=1}^{n} MS_{lib,i} \times MS_{temp,i}}{\sqrt{\sum_{i=1}^{n} (MS_{lib,i})^2} * \sqrt{\sum_{i=1}^{n} (MS_{temp,i})^2}}$$

In eq. 4, *n* is the continuous number of even m/z-values (ranging from 1 to an all-inclusive maximum of 5000) in the current mass spectrum MS_{temp} and the currently evaluated mass spectrum in the library MS_{lib}. This score was calculated for all possible pairs of library entries and unidentified mass spectra as shown in [35, 37].

Eq. 5 $$score_{MS+RI} = 1 - \frac{(1 - score_{MS}) + abs(\frac{RI_{temp} - RI_{lib}}{RI_{lib}})}{2}$$

In eq. 5, we defined a combination of differences in RI and MS match quality by setting the $score_{MS}$ calculated in eq. 4 against the difference between the RI in the library RI_{lib} and the RI calculated for the unidentified mass spectrum RI_{temp}. The obtained $score_{MS}$ was further offset with the RI-match to another score ($score_{MS+RI}$), as shown in eq. 5. To ensure that only database entries with RI variances of +/- 30 compared to the peak under consideration were taken into account, a Heaviside function was multiplied with the score as shown in eq. 6 and described in [35, 37].

Eq. 6 $$f(|RI_{temp} - RI_{lib}|) = \begin{cases} 0, if\ |RI_{temp} - RI_{lib}| > 30 \\ 1, if\ |RI_{temp} - RI_{lib}| \leq 30 \end{cases}$$

The resulting scores are thereby found to be between 0 (no match) and 1 (absolute match). For the compound detection and the final compound list, the minimum score for the proposition of an analyte's identity can be chosen freely (e.g. 0.8). All unknown mass spectra (peaks) of the sample chromatograms went through this procedure.

Compound determination in model whisky and samples

For the qualitative determination of compounds in the model whiskies, one blank sample per model was considered. Thereby, analytes were detected in the blank chromatograms (blank Twister® without model whisky extraction) as well as in the Twisters® used for analyte extraction from the model whiskies with a threshold score of 0.8 for compound detection (cf. equation 5). Subsequently, all compounds that were noted in both the blank and model whisky Twisters® showing peak area ratios (peak area in model whisky / peak area in blank) smaller than 3 were subtracted from the model whisky compound list.

The 16 sample chromatograms were processed following the above-described procedure for compound detectionapplying a threshold of 0.8 with no blank subtraction.

Statistical data evaluation

For the statistical evaluation of the sensory data, XLSTAT (Excel, Microsoft Cooperation, Redmond USA) as well as MATLAB (R2022a, The MathWorks Inc., Natick USA) was used. For the statistical analysis of the raw sensory data, they were split into qualitative (according to "Check all that apply", CATA, data) and intensity (RATA) data and processed separately similar to the studies published by Vidal et al. [21]. The CATA data was treated with the "CATA data analysis tool" in XLSTAT (Excel, Microsoft Cooperation, Redmond USA).

The statistical analysis of analytical data and the correlation of sensory and analytical data was conducted in MATLAB (The MathWorks Inc., Natick USA). For the task of classifying whisky samples by type (Scotch or American), we used three non-exclusive sets of sensory and analytical data. (1) A combination of all RATA data (sum of ratings divided by participant counts) for 40% and 20% ABV for all 17 sensory attributes; (2) A list of relative peak areas (quantified by their abundance relative to 4-chloro-2-methoxyphenol) over all molecules detected in each whisky sample; (3) A combination of (1) and (2). We then used each dataset in 5000 repetitions of training and testing a linear discriminant analysis (LDA) approach. Each of the repetitions featured a different, randomly drawn subsample of the full set of 16 samples, split into 13 samples for training and 3 for testing. During each the training, a five-fold cross-validation was performed. There are 560 possible subsets of 13 in a full set of 16 ($\frac{16!}{13!*3!}$). For each repetition, we calculated the accuracy of the cross-validated training as well as the test accuracy. The final percentage of correct classifications was then calculated as repetitions in which test accuracy was 100%, divided by number of repetitions.

Results and discussion

Sensory evaluation

Assessment of the parameters applied for the sensory evaluation

Corresponding to the goal of a fast and informative procedure for the analytical and sensory evaluation of whisky, a rapid sensory method using the RATA principle [21, 38] was chosen for the sensory testing. Within this trial, 16 different whiskies with different alcohol contents, resulting in a total of 40 samples were evaluated orthonasally by 11 panellists within 4 sessions each. Therefore, the evaluation of 40 samples in total took around two hours for each participant or 22 participant hours in total.

In order to obtain insightful information and to work out differences and similarities in the aroma characteristics of different whiskies by the RATA method, the selection of appropriate attributes for the sample description is of utmost importance. Within the sensory evaluations, all attributes have been used to describe the samples. The most often used attribute was fruity (156 times), while the attribute coconut-like was selected the least (29 times). This shows that all attributes were applicable to some of the samples and that the extent of their use differed. The option to state "other" attributes was used 33 times by 9 panellists. However, no statistical relevance could be detected between the attributes and the samples they were used for. Specifically, 9 of those attribute mentions (27.3 %) came from one participant, and 51.5 % of all alternative mentions came from just 3 participants. Taken together, these findings show that the selection of attributes was appropriate for the sensory description of the present whisky samples.

Qualitative sensory data

For the evaluation of sensory data, the whisky samples at 20 and 40 % ABV were considered. Data obtained by sensory analysis was treated as described above (cf. “statistical data evaluation”). The qualitative sensory data obtained by applying the RATA-method corresponds to check-all-that-apply (CATA) data and was used for the mapping of the whisky samples based on their perceived aroma characteristics. Following statistical data processing including the determination of significant attributes for the sensory evaluation and principal coordinate analysis (PCoA), the whisky samples (20 and 40 % vol.) could be mapped together with their descriptors. Caramel / cream caramel / toffee, vanilla, (canned) peach, phenolic, smoky, fruity, flowery and (fermented) apple / cider were identified as significant attributes. PCoA and mapping of the Scotch and American whisky samples allowed the representation of the main characteristics of the samples within a sensory map. Principal coordinates (PCo) 1 and 2 represent ca. 75 % of distance within the sample set and therefore the major differences can be accounted for by PCo 1 and 2. As can be seen in Figure 1, the two sample groups (Scotch and American) occupy different parts of the map and can therefore be distinguished based on their position within the plot. However, there is still a significant intergroup variation within the two sample sets, which makes the differentiation more difficult. This variance for example becomes obvious for the attributes phenolic and smoky. These features are characteristic for Scotch and not for American whiskies, however, they do not apply to each of the Scotch samples.

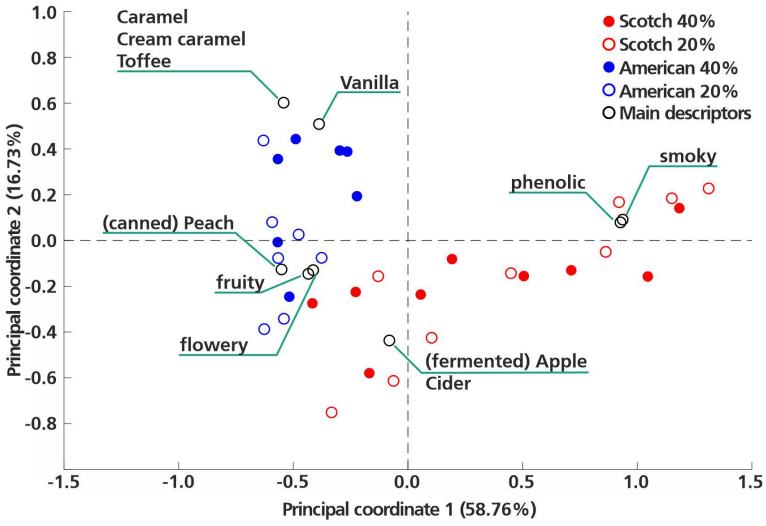

Fig. 1 Sensory mapping of 16 whisky (9 Scotch, red and 7 American, blue) samples at two different ABV levels (20 %, dot and 40 %, circle) based on the evaluation of significant sensory attributes (main descriptors, black circles).

Differentiation between Scotch and American whiskies

A linear discriminant analysis (LDA) was performed on the sensory RATA data (normalized to participant count) to gain further insights into the differences and similarities between the samples. For this purpose, there was one data point for each whisky comprising information for both the 20 and 40% ABV level, as these are no independent samples. Based on this, we were able to categorize the aroma characteristics of the samples in Scotch and American Whiskies with high accuracy. Within 5000 repetitions, 97.86 % of classifications were correct. As illustrated in Figure 2, it could be shown that the attribute caramel / cream caramel / toffee-like could thereby be used as a reliable predictor for the differentiation.

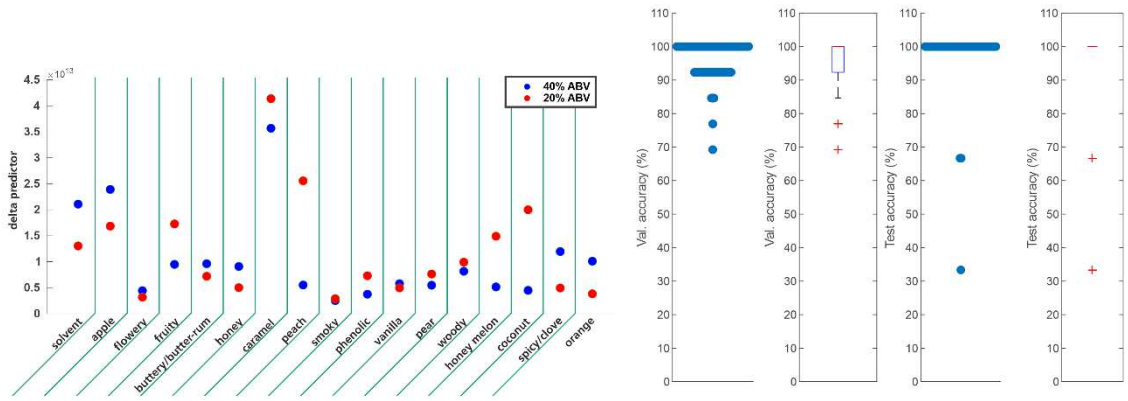

Fig. 2 Linear discriminant analysis of the sensory data. Left: Relevance of single sensory attributes as predictors for the categorization. Right: Differentiation between Scotch and American whisky.

Analysis of model whiskies

To evaluate the extraction efficiency of the applied sampling method as well as to test the reliability of the automated processing, two model whiskies were analyzed. The persons handling the automated processing program for the analytical data were not informed about the compositions of the model whiskies at first to avoid any influencing factors. The models contained 27 (model whisky 1) and 26 (model whisky 2) typical whisky aroma compounds in varying concentrations (cf. table 1). Applying a threshold of 0.8 for the total score (eq. 5) and a ± 30 penalty for the RI value (eq. 6) for the determination of analytes, 21 out of 27 compounds (model whisky 1) and 21 out of 26 compounds (model whisky 2) were eventually detected correctly after blank subtraction (as described above). The internal standards 4-chloro-2-methoxyphenol and undecane were detected in both model whiskies with scores > 0.9. In model whisky 1 all added analytes were detected except for *β*-damascenone, 2-methylbutanol, 4-methylphenol, 4-ethylphenol and the two aldehydes 2- and 3-methylbutanal. An overview on the detection of analytes in model whisky 1 is shown in figure 3. Instead of 4-methylphenol and 4-ethylphenol, the respective C3-isomers 3-methylphenol and 3-ethylphenol were reported as best matches. This might be attributed to the fact that the isomers show similar RI values and mass spectra. Consideration of the second-best hit showed that 4-methylphenol was listed right after 3-methylphenol with a slightly lower score (0.913 and 0.916). 2-methylbutanol that was not reported using the automated processing, while 3-methylbutanol with similar RI-value and mass spectrum was detected at multiple retention times. The second-best match, however, was not 2-methylbutanol. *β*-Damascenone was not reported by the automated processing which might be because of low analyte concentration or extraction efficiency during the SBSE. It can be assumed that the assessment and detection of these two analytes is impeded, especially at low concentrations. Processing of chromatographic data of model whisky 2 lead to the detection of 21 out of 26 analytes added to the model whisky, 2-methoxyphenol, furfural, 2- and 3-methylbutanal and phenol were not reported. The former is a phenolic compound with a polar hydroxyl- and methoxy group showing a log $K_{O/W}$ value of around 1.3 and boiling point of 205 °C [44]. Relatively high polarity as represented by a low log $K_{O/W}$ might result in poor extraction by the unpolar PDMS sorbent. As the compound was detected in model whisky 1, however, it could be shown that that the applied method is suitable for higher analyte concentrations (0.54 µg/mL vs 3.36 µg/mL). Other phenolic compounds 4-allyl-2-methoxyphenol and 4-methylphenol were assigned correctly in model whisky 2. Phenol and furfural were only detected in the original model whisky 2 data before blank subtraction. As both analytes also occur in the blank chromatograms in similar intensities, they were subtracted from the

model whisky results. The detection of these analyte in the blank analyses might be due to contaminations, e.g. in the chromatographical system as well as the high sensitivity of the applied compound detection procedure. It should be noted, that apart from the compounds that were intentionally added to the model whiskies, many other compounds were detected applying the automated processing on the chromatographic data. This means that there is generally a high background noise that is sensitively detected by the automated processing.

Taken together, the majority of analytes were extracted from and successfully detected in the model whiskies. However, for a few compounds the applied analytical methods and subsequent automated data processing is not yet capable to provide a reliable detection and compound assignment. This is for example the case for 2-methoxyphenol and β-damascenone, which might only be detectable at higher concentrations. For other analytes, a clear distinction between isomers could not be achieved. Therefore, it can be assumed that in some cases, the extraction efficiency of the applied method can be regarded as the limiting factor, while for other compounds, the automated processing needs further tuning. This might be achieved through less sensitive peak detection algorithms to exclude noise and the training of models (e.g. decision trees) for the correct identification of isomers based on differences in mass spectral data. For this, it is likely that few m/z-peak ratios specific to an isomer would be sufficient. Furthermore, the results show, that a score of 0.8 and RI value penalty of ± 30 is appropriate for the compound detection in the present samples.

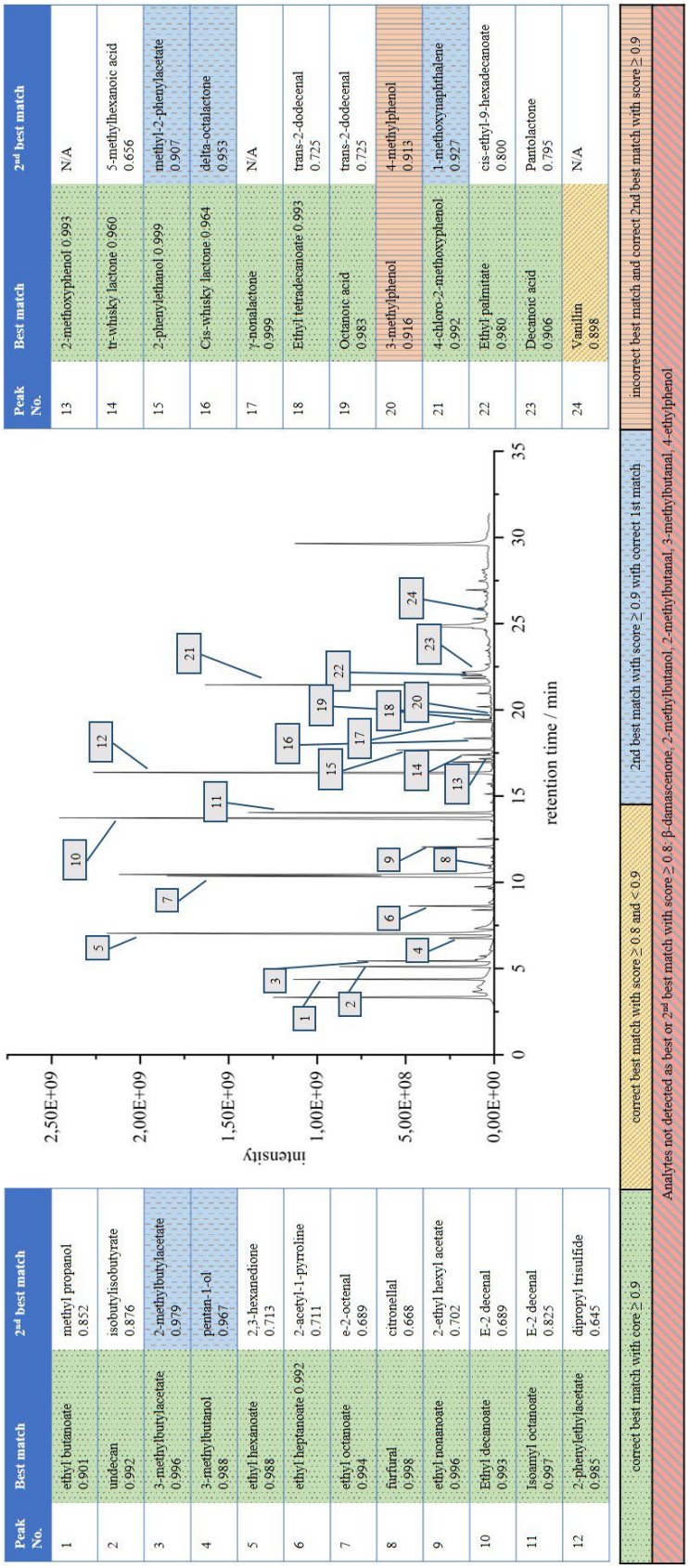

Fig. 3 correctly assigned analytes in model whisky 1. All as "best match" assigned analytes present in model whisky 1 as well as one analyte suggested as 2nd best match are shown together with the respective 2nd best matches, chromatogram was considered before blank subtraction. If analytes were detected at several retention times, matches with highest peak areas were considered. Analytes present in the model whisky that have not been detected, are indicated at the bottom.

Detection of volatile compounds in whisky samples

Applying a score of 0.8 and a RI value penalty of ± 30 a chromatographic data set obtained from 16 different whiskies was processed for an automated compound detection. As described above, this includes an automated process for compound detection and identity proposition based on MS and RI data (eq. 5 and 6) without the consideration of odor activity or quality, the direct comparison with reference measurements or further evaluation by experts. The results discussed here refer to the analytes assigned as best matches following the automated compound detection based on RI and MS characteristics in comparison to an in-house built analyte database. In all whisky samples, the two added internal standards undecane and 4-chloro-2-methoxyphenol were successfully detected. Between 89 (Scotch sample S07B400) and 153 (Scotch Sample S04A400) analytes were proposed in the whiskies. In total, 279 compounds were reported for the 16 samples (cf. table S5), including internal standards. However these were not unequivocally identified and should be considered as compound suggestions. This might become obvious especially for some compounds that also occur in any blank chromatograms (for model whiskies or samples as described above), have comparably low confidence values (< 0.9) or are not reported as typical whisky compounds (cf. table S5). Nevertheless, among these, there were many compounds that have previously been reported for whisky [5, 6, 8, 9].Among the compounds that were reported in all 16 samples (cf. table S4) following the described compound detection procedure were decanoic acid, ethyl decanoate, 3-methylbutanol, dodecanoic acid, ethyl octanoate, (9*Z*)-hexadec-9-enoic acid, octanoic acid, 2-phenylethyl acetate, ethyl dodecanoate and ethyl hexanoate. These analytes belong to those showing the highest relative areas in relation to 4-chloro-2-methoxyphenol, however, this is no indication of their concentration ratios or influence on the overall whisky aroma. Typical whisky volatiles [4–6, 9] found in the samples are for example 4-hydroxy-3-methoxybenzaldehyde (vanillin), *cis/trans*-5-butyl-4-methyloxolan-2-one (whisky lactone), 2-methoxyphenol, 2-phenylethanol, 4-allyl-2-methoxyphenol, as well as further ethyl and isoamyl esters. Vanillin was proposed for all American whisky samples and 4 Scotch, *cis*- or *trans*-whisky lactone was detected in all 16 samples, while 4-allyl-2-methoxyphenol (eugenol) was reported for all American and 3 Scotch whiskies. Surprisingly, 2-methoxyphenol (guaiacol) was detected in all American and only 5 Scotch whiskies. 2-Phenylethanol- was detected in all 16 samples. Apart from the already mentioned ethyl esters, further examples of this compound class are ethyl heptanoate, ethyl butanoate and ethyl nonanoate. Other esters proposed for some samples include isopentyl decanoate, isoamyl hexanoate, isoamyl octanoate and isoamyl acetate. Some analytes that were not detected in the model whiskies (before or after blank subtraction), were however reported for at least one whisky sample. These include 2-methylbutanol, *β*--damascenone and 3-methylbutanal. Several phenolic compounds, such as 4-ethyl-2-methoxyphenol, 3- or 4-methylphenol and 3- or 4-ethylphenol were also proposed for some samples. Apart from whisky lactone, other representatives of the group of lactones as for example *γ*-decalactone and *γ*-nonalactone- were reported. Apart from a wide spectrum of analytes regarding functional groups and physico-chemical properties, a variety of different odor qualities is represented by the detected analytes, characteristic for whisky [1, 4, 5]. This for example includes compounds with a fruity (ethyl hexanoate, isoamyl acetate), flowery (2-phenylethanol, 2-phenylethyl acetate), phenolic/smoky or burnt (2-methoxyphenol, 4-methylphenol, 4-ethylphenol) or coconut –like (*γ*-nonalactone-, whisky lactones) aroma perception (aroma qualities obtained from in-house database and [4, 5]). It has to be noted that the molecules named here and listed in table S4 are only compound propositions based on the automated detection procedure using RI and MS data and an in-house database. This means that this is neither an unequivocal compound identification nor a complete list of aroma-active volatile compounds present in the

whisky samples. This is due to several factors, including that the database used is not complete and includes compounds with similar RI and MS data, impurities in the sampling or chromatographic system might be included in the compounds list. Therefore, some compounds detected in the samples are very commonly found in whisky or foodstuffs in general, while others seem rather unlikely. For an unequivocal compound identification, a more thorough analysis procedure, including reference measurements and consideration of odor qualities would have to be applied. However, this was not the scope of this research.

Classification of Scotch and American whisky based on analytical results

We found that several molecules could be used in a binary decision process to distinguish between the two whisky types. Inspection of the data showed that two molecules were only proposed for Scotch and for all Scotch samples, namely heptanoic acid and methyl decanoate, while two other compounds, 3.7-dimethyloct-6-en-1-ol (citronellol) and 5-methyl-2-propan-2-yl-cyclohexan-1-ol (menthol) were detected exclusively in all American whiskies. Despite finding the molecules menthol (exclusive to American whisky) and heptanoic acid (exclusive to Scotch) in the blank chromatogram, the peak areas were consistently far lower than in sample chromatograms. Menthol peak area in the blind chromatogram was 5.9 % of the average peak area in all American samples, while heptanoic acid peak area equalled 11% of the average in all Scotch samples. We therefore still propose these molecules to be valuable in the classification of the whisky types. This data-driven determination of exclusive molecules that can be used for distinction is promising, while its validity still needs to be evaluated more rigorously. As only a small number of samples (9 Scotch, 7 American Whiskies) was analyzed, the use of these compounds as distinct predictors for the two whisky types has to be further investigated. According to literature findings, methyl decanoate has so far been detected in Scotch whisky [2, 7, 9], no report on methyl decanoate in American whisky has been found to our knowledge. González-Arjona et al. [25] investigated three different whisky types (Scotch, Irish and Bourbon) via GC-MS analysis of the solvent extracts and evaluated different pattern recognition procedures for their classification. After conducting a PCA on their data, they identified heptanoic acid amongst others as one of the features contributing the most to the first two PCs. However, they did not indicate in which samples the compound was predominantly found [25]. While heptanoic acid and methyl decanoate have been reported for whisky [2, 7, 9], citronellol and menthol do obviously not represent typical whisky components. Interestingly, three of the four molecules (except heptanoic acid) were also among the most decisive factors in the LDA-mediated classification (see Figs. 4 & 6). Apart from that, it could be seen that among the compounds that were only detected in Scotch samples, but not necessarily in all of them, are several phenolic compounds. This is in accordance with previous reports, where especially for peated whisky, different phenolic compounds were found [4, 45].

Furthermore, an LDA was conducted based on the analytes detected in the 16 whisky samples to see if the two kinds can be classified based on their automatically generated volatiles lists as described above. For this purpose, all unique analytes (analytes could only appear once in each sample) were considered in a semi-quantitative manner by calculating the relative peak area to the internal standard 4-chloro-2-methoxyphenol. Figure 4 shows the main influences for the classification as determined by LDA. Nine molecules with delta predictor values above 2 are labelled as they showed the highest influence among all molecules. These were (*E*)-oct-2-enal, (*E*)-dec-2-enal, *β*-damascenone, 4-allyl-2-methoxyphenol (eugenol), isoamyl decanoate, citronellol, whisky lactone, myrtenol, menthol and methyl decanoate. While some of these compounds like eugenol, whisky lactone, isoamyl

decanoate, β-damascenone- and methyl decanoate have been reported for different kinds of whisky [2, 5–7, 9], the other compounds do not represent typical whisky volatiles as shown by literature. However, as noted above, compounds have not been identified unequivocally and there is still a reasonable chance of misdetection.

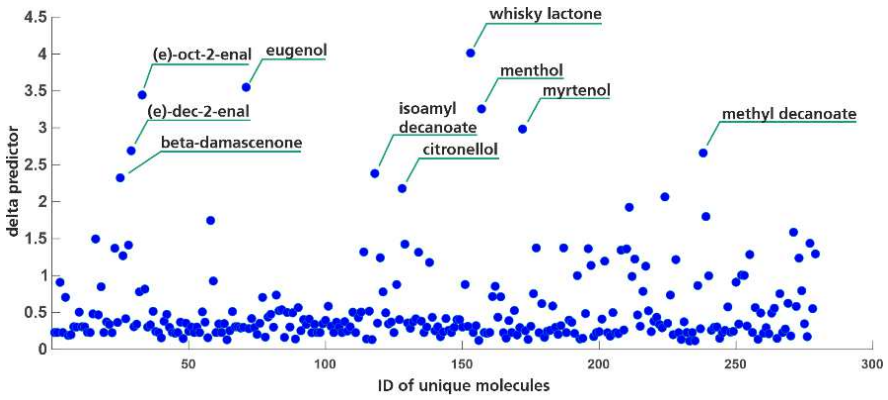

Fig. 4 Determination of potential predictors for the classification of Scotch and American whisky based on the delta predictors of an LDA using all detected whisky volatiles

The delta predictor plotted in Figure 4 is a representation of how much of an influence each individual molecule exerted on the classification. The compound with the highest value is whisky lactone (sum of *trans* and *cis* whisky lactone), which was detected in all whisky samples. However, the relative peak areas (compared to the internal standard 4-chloro-2-methoxyphenol) indicated that the analyte was present in higher amounts in the American whiskies.

LDA on analytical data performed by the procedure outlined above, resulted in 80.74 % prediction accuracy for the classification between Scotch and Bourbon based on the detected volatiles (fig. 5 A). This relatively low value might be ascribed to several causes: In the whisky samples, a significant number of minor compounds were detected and there was no subtraction of a blank chromatogram. Therefore, many compounds that are not relevant for the classification of whiskies or occur only in traces or as noise are also considered here. This might be a reason for the occurrence of rather untypical whisky volatiles as predictors as well as low prediction accuracy. A high number of predictors in combination with a low sample count further poses the risk of overfitting in LDA. This concern was addressed by introducing a preceding PCA keeping only 4 main components, which led to an accuracy of 96.98% (fig. 5 B). To avoid this issue, further thresholds could be set, e.g. in relation to minimum peak area or compound purity to improve the processing of GC-MS data. Furthermore, low classification accuracy might be attributed to the quality of the generated GC-MS data. As compounds of various different compound classes and physico-chemical features appear in a wide concentration range, their sampling and analysis must be suitable to detect differences between the samples. As analyte extraction was conducted using a PDMS Twister®, extraction efficiency for polar compounds present in lower concentrations might have been insufficient. Furthermore, it could be seen, that especially ethyl esters such as ethyl decanoate and ethyl dodecanoate were extracted in high amounts from all samples, irrespective of the type of whisky. Taken together, the samples showed huge similarities especially for the major peaks detected in the chromatograms. For more detailed information on analytical differences between the samples, other sampling

strategies, e.g. the use of other sorbent phases, should be considered. Furthermore, the use of specifically designed databases for whisky samples as opposed to general in-house (aroma) compound database that was used for this study could refine the analyte list. This would put a stronger focus on analytes relevant for whisky, as suggested by Grasskamp et al. [35]. Apart from that, it must be considered that the proposed strategy aims at delivering a quick overview on the samples and (aroma-active) volatile compounds present without the validation of compound identities. To obtain a reliable and validated list of (aroma) compounds in the samples, which is out of this research's scope, a thorough analysis procedure for unequivocal compound identification is usually applied [5, 46].

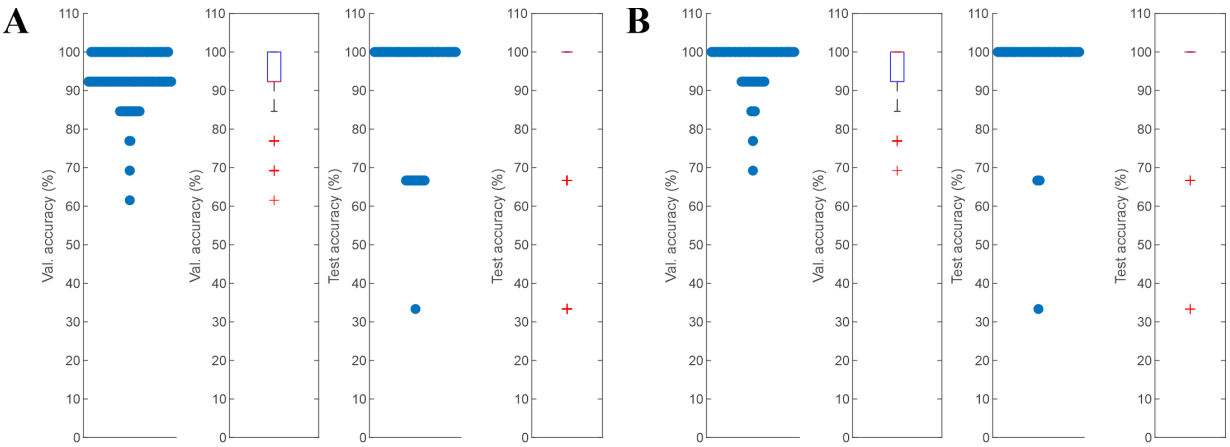

Fig. 5 Linear discriminant analysis for the classification of 16 whisky samples based on analytical data, 5000 repetitions using a training set of 13 and test set of 3 samples. A) without and B) with preceding PCA keeping only 4 main components, leading to accuracies of 80.74% and 96.98 %, respectively.

A third approach showed a classification accuracy of 94.2 % with analytical data, but with all molecule amounts turned to 1 (resulting in a binary, qualitative analytical matrix), without the consideration of (relative) peak areas. The results of this are shown in the supplementary material (fig. S2). This analysis put a heavy focus on those molecules that were only present in one of the two whisky types. As whisky lactone showed a clear and systematic distinction in detected amounts between the two whisky types, but was found in each sample, it had no influence in this type of qualitative analysis. Furthermore, many of the molecules determined as having the highest influence on the separation were those detected with low confidence values close to the cut-off of 0.8. This may point towards closely related metabolites of whisky specific molecules that were not present in our target database, or towards problems in purity of trace compounds essential for the distinction.

Comparison of the use of sensory and analytical data for whisky classification

Eventually, a LDA was conducted using both the analytical and sensory data in combination. In agreement with both the LDA from sensory as well as from analytical data, the classification accuracy of the combinatory LDA was found to be between the two single LDAs. Within 5000 repetitions, correct classification was achieved in 87.96 %, results are shown in figure 6.

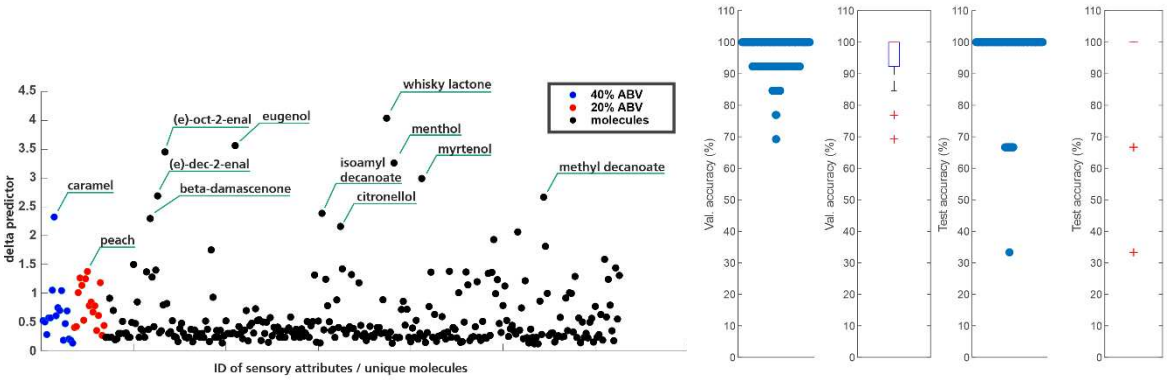

Fig. 6 Linear discriminant analysis for the classification of 16 whisky samples based on analytical and sensory data in combination, 5000 repetitions using a training set of 13 and test set of 3 samples.

While significantly more predictors showed an influence above 2.0 (delta predictor) for the analytical data, the sensory attribute "caramel" showed by far the highest value among all attributes for the sensory data. Even so, the classification of whisky types applying LDA was more accurate using sensory data (97.86 %) than analytical data (80.74 %). From this it can be concluded that the sensory attributes used are more distinctive for the two kinds of whiskies than the compounds detected using the automated processing following SBSE-GC-MS analysis. As discussed above this might be due to the large number of analytes including minor compounds and noise detected in the whisky samples. Interestingly, while the most distinctive sensory attributes according to the LDA were caramel and peach, the odor qualities of the descriptor analytes range from fatty ((E)-oct-2-enal, (*E*)-dec-2-enal), grape-juice / cooked apple like (*β*-damascenone), eucalyptus-like (menthol, myrtenol), soapy (methyl decanoate), clove-like (eugenol) to lemongrass-like, rose-like (citronellol) and coconut-like (whisky lactone) (aroma qualities obtained from in-house database and [5]). Therefore, for an automated evaluation on how certain molecules might define or influence the sensory characteristics of a sample, other features might have to be taken into account. For odorous compounds it has to be considered that their concentration within the sample does not necessarily correlate with their impact on the overall aroma profile as they might show high odor thresholds and therefore lower odor activities as compared to other compounds. Thus, even compounds present in low concentrations might have a significant influence on the aroma profile of the whisky. Within comprehensive aroma or odorant analyses, e.g. for the determination of key aroma compounds, often a correlation between the most potent odorants (as characterized by high flavor or odor dilution factors) and the predominant sensory attributes can be observed [11, 46, 47]. For this purpose, odor qualities as well as odor thresholds and resulting odor activity values [11, 20, 48] for the detected compounds could be included in the presented automated processing. This would not only allow for a potential characterization of the sensory profile but also combine analytical and sensory classifications of the samples based on solely analytical data.

Based on the two datasets described here, the use of sensory data and analytical data are both suited for the classification of Scotch and American whisky. However, even if a fast sensory method (RATA) was applied, sensory evaluation is a time-consuming step, particularly for large sample sets. Especially for classification matters, more efficient methods based on analytical data are more appropriate. Therefore, analytical data generated by high-throughput GC-MS treated by automated processing might soon provide the most efficient method for this objective.

Recent research shows that the classification of samples based on analytical data on volatiles is a promising tool for the classification of different kinds of samples. This also applies for whisky, e.g. in relation to quality gradings [26], type or origin [24] as well as authenticity [3, 49]. Zhang et al. [24] investigated the use of an e-nose for the differentiation between Whiskies of varying brands, origins and styles (three different blended malt und three single malt whiskies). Based on chromatographic data obtained by headspace SPME GCxGC-ToFMS, single malt whiskies and blended whiskies could be clustered via PCA analysis. Furthermore, differences regarding the regions of origin were illustrated through three clusters by PCA. However, the first two PCs only accounted for 53% of the overall variance and only a small sample set (n=6) was considered. Applying different classification methods on the e-nose data, three classification problems were approached: distinguishing all 6 whisky samples brand names, classification through regions of origin and classification through whisky style. For each classification problem, a specific combination of classification models was chosen based on the results during the training. Two out of the six whisky samples were then selected for a field trial of the e-nose, resulting in a total of 58 datasets. Classification correctness was 96.15%, 100% and 92.31% for brand name, region and style, respectively. This study shows the use of classification methods on analytical data based on the volatiles profile of whisky, however it must be noted that only a small number of samples considered and the two test samples for the field trial were already included in the model training [24]. Wiśniewska et al. [50] investigated the classification of 11 whisky samples of different origin (Ireland, Scotland, Spain, Tennessee and Kentucky) following different analysis approaches. Samples were analyzed in duplicate by headspace MS, UV-Vis, Infrared-Attenuated Total Reflectance (IR-ATR) and IR-Transmission (IR-T). Partial Least Square Discriminant Analysis (PLS-DA) was applied for discriminating the samples based on their origins. Best classification results were obtained by using HS-MS data, suggesting that the main difference between the whisky types can be found in their aroma profile, according to the authors. Furthermore, it was indicated that further discriminations could be made within each group [50]. A comprehensive study for the classification of whisky samples based on GC-MS data was conducted by Stupak et al. [49]. A total of 191 whisky samples, including 71 malt whiskies, 77 blended Scotch whiskies, 20 samples previously identified as fake and 23 additional malt whiskies maturated in more than one type of cask. Comparing two different sampling strategies, headspace SPME and extraction with ethyl acetate, the latter proved more suitable to solve the classification problems. More details on the sample composition was delivered through solvent extraction as also semi-volatile compounds were detected. The samples were successfully classified regarding the cask used for maturing (bourbon vs. bourbon and wine cask) and characteristic markers could be identified for the differentiation based on PLS-DA. Similarly, a separation between blended, premium blended and malt whiskies could be achieved. Application of PLS-DA led to the determination of six compounds as markers responsible for the differentiation between malt and blended whisky. Furthermore, separation between genuine and fake samples was achieved via PCA analysis. This also allowed for the identification of marker compounds for whisky authenticity via PLS-DA [49]. González-Arjona et al. [25] investigated the use of four different pattern recognition procedures for the classification of 52 whisky samples (single malt Scotch, bourbon and Irish whisky). Data was obtained by solvent extraction with dichloromethane followed by GC-MS analysis and analyte identification with the NIST library. This way, 28 compounds were considered for the classification of the 52 samples. The best results were obtained by ANN (multilayer perceptrons, MLP and probabilistic neural networks, PNN). LDA showed weaker performance for solving the classification problem as some class overlappings could be observed [25].

As suggested within the present research paper, the use of chemometrics might not only be advantageous for the classification of native sample properties, like origin, type, and authenticity. Moreover, such methods might also be employed for sensory evaluation and to even estimate aroma profiles based on analytical data. Liu et al. [51] for instance, investigated the sensory and chemical profiles of milk samples fermented with different bacteria. First, sensory analysis was conducted to determine the major sensory attributes, leading to the classification into five different groups. Volatile profiles of one sample per group were determined through analyte identification following headspace-GC-Ion mobility spectrometry (IMS) and headspace SPME-GC-TOFMS analysis. PCA analysis and OPLS-DA were then used for discriminating the aroma types and determine six potential indicators for different aroma characteristics of fermented milk samples [51]. Within a study conducted by Zhu et al. [26], 143 end-fermented Sauvignon blanc wine samples were analyzed sensorially to determine their sensory gradings as well as analytically via HS-GC-IMS. Based on a non-targeted approach, the volatiles detected by GC-IMS were used for the classification of the samples in relation to their sensory gradings. PCA using all peaks irrespective of the analyte identity, was not suitable for the clustering of the samples under investigation with PC 1 and PC 2 explaining only 36.48% of the total variance. Among the six machine learning models investigated, artificial ANN delivered the most promising results with a prediction accuracy of 95.4 % linking analytical data to sensory quality gradings [26].

The prediction of whisky aroma profiles based on analytical data using chemometrics or even machine learning models would be beyond the scope of this paper. However, the present article presents the first and promising steps for the implementation of a fast and efficient platform for the generation and handling of analytical and sensory data for aroma analysis.

The use of modern data science and machine learning has become an integral part in analysis of MS with different modes of chromatography (liquid/gas), showing how an approach such as ours may well be amended to further improve outcomes [52]. Several as yet unsolved issues can be addressed with approaches such as this. Among these, taking into account what margin of error may be expected from different detectors is an inherently fitting problem for highly performant data analysis methods and will not be solved by manual work due to the complexity. This necessitates a systematic large-scale investigation of mass spectra aided by efficient approaches with high potential to aid in human decision-making such as the one presented here.

Summary and conclusions

Within this paper, the analytical as well as sensory evaluation of 16 different whisky samples was presented. Focus thereby laid on the evaluation of efficient analysis methods and data processing for both chemical and sensory evaluation. For the chemical analysis, SBSE followed by GC-MS analysis was applied and an in-house developed tool for analyte detection was used. To evaluate the analytical procedure, two model whiskies containing typical whisky aroma compounds were prepared and processed comparably to the genuine samples. Sensory data was obtained by applying the RATA method determining the most prominent aroma impressions for the samples at different alcohol levels (original if > 40%, 40% and 20%). Statistical methods were applied to gain deeper insights into the generated data and to compare the two approaches for a classification problem (Scotch vs. American whisky).

Sensory evaluation and subsequent statistical analysis showed that from the 17 attributes offered, the following 8 contributed significantly to the overall differentiation of samples: caramel / cream caramel / toffee, vanilla, (canned) peach, phenolic, smoky, fruity, flowery and (fermented) apple / cider. Following PCoA, the samples could be clustered in two groups: Scotch and American whisky, however there was a large intergroup variance, especially for Scotch whisky. Performing an LDA, the samples were classified with high accuracy (97.86%) into Scotch and American whisky. The attribute caramel / cream caramel / toffee was thereby identified as a reliable predictor for the differentiation of Scotch and American whisky in the present sample set.
To evaluate the analytical procedure, including SBSE GC-MS sample analysis as well as automated processing and compound detection and identity proposition, two model whiskies containing typical whisky aroma compounds were analyzed. For each model, 21 out of 27 and 26 compounds respectively as well as the two internal standards added, were detected correctly through the automated processing. This suggests that the analytical procedure, including sample analysis as well as processing, are suitable for the investigation of aroma compounds in whisky samples. Some analytes, however, were not detected in their given concentrations while for others, isomers were suggested. Therefore, the procedure needs further optimization regarding i) the sampling strategy to cover a wider range of analytes and concentrations and ii) the analyte identification, e.g. in regard to the differentiation between isomers. The same procedure was then applied to the 16 whisky samples (40 % ABV) and lists of detected molecules as well as their peak areas (relative to the internal standard 4-chloro-2-methoxyphenol) were generated. According to these, a large number of aroma compounds typically found in whisky were detected in the 16 samples. An LDA was then conducted on the data to evaluate if the samples can be classified into Scotch and American whisky based on the analyte lists. Results showed an accuracy of 80.74% for the semi-quantitative data (including relative peak areas) and 94.2% with qualitative data only, while a preceding PCA keeping four main components (explaining >95% of observed variance) increases these values to 96.94% and 99.92%, respectively. A PCA on sensory RATA data did not improve results. The qualitative approach thereby puts focus on the molecules only present in one of the two whisky classes. Compared to sensory data, use of the analytical data the proposed classification problem offers similar accuracy. The analytical procedure that was applied for the present samples therefore needs optimization, e.g. in regard to analyte extraction from the sample matrix but also their identification during data processing. As most distinctive analytes (descriptors) for the differentiation between samples, ten molecules were assigned. Those were (*E*)-oct-2-enal, (*E*)-dec-2enal, *β*--damascenone, menthol, methyl decanaote, isoamyl decanoate, eugenol, myrtenol, citronellol and whisky lactone with the highest impact. However, it has to be noted that only some of these molecules represent typical whisky compounds according to literature data. As only RI and MS data were taken into account for the automated data processing without the consideration of odor qualities and reference measurements to validate analyte identities, it has to be considered that some compounds might have been incorrectly assigned. Furthermore, many of the proposed compounds might be traces or impurities as also in the blank analyses a large number of compounds was detected.

Taken together, our investigations show the potential of efficient sensory and analytical procedures for the evaluation of whisky samples based on their aroma and volatiles profile. A simple sample workup and analysis procedure (SBSE GC-MS) including the automated analyte detection and proposition as well as a rapid sensory method (RATA) were tested and evaluated in combination with statistical methods for their potential to solve a simple classification problem. This represents a first step towards a comprehensive platform for fast and efficient

aroma analysis. Thereby, more sophisticated classification questions, e.g. in relation to aroma profiles of food samples based on analytical data, can be approached. For this purpose, further investigations can be conducted to adjust and test analytical parameters for analyte extraction and instrumental analysis as well as the data processing, analyte identification and the consideration of compound specific properties, such as odor activity values.

Declarations

Conflict of Interest

No conflict of interests.

Compliance with ethical standards

The authors have no relevant financial or non-financial interests to disclose. Informed consent was obtained from all subjects participating in the sensory study.

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Data availability

Data generated during the current study are available from the corresponding authors on reasonable request.

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References

1. Lee K-YM, Paterson A, Piggot JR. Origins of Flavour in Whiskies and a Revised Flavour Wheel: A Review. Journal of the Institute of Brewing. 2001; https://doi.org/10.1002/j.2050-0416.2001.tb00099.x
2. Daute M, Jack F, Baxter I, Harrison B, Grigor J, Walker G. Comparison of Three Approaches to Assess the Flavour Characteristics of Scotch Whisky Spirit. Appl. Sci. 2021; https://doi.org/10.3390/app11041410
3. Wiśniewska P, Dymerski T, Wardencki W, Namieśnik J. Chemical composition analysis and authentication of whisky. J. Sci. Food Agric. 2015; https://doi.org/10.1002/jsfa.6960
4. Jeleń HH, Majcher M, Szwengiel A. Key odorants in peated malt whisky and its differentiation from other whisky types using profiling of flavor and volatile compounds. LWT. 2019; https://doi.org/10.1016/j.lwt.2019.02.070
5. Poisson L, Schieberle P. Characterization of the Most Odor-Active Compounds in an American Bourbon Whisky by Application of the Aroma Extract Dilution Analysis. J. Agric. Food Chem. 2008; https://doi.org/10.1021/jf800382m
6. Ferracane A, Manousi N, Tranchida PQ, Zachariadis GA, Mondello L, Rosenberg E. Exploring the volatile profile of whiskey samples using solid-phase microextraction Arrow and comprehensive two-dimensional gas chromatography-mass spectrometry. J Chromatogr A. 2022; https://doi.org/10.1016/j.chroma.2022.463241

7. Câmara JS, Marques JC, Perestrelo RM, Rodrigues F, Oliveira L, Andrade P, Caldeira M. Comparative study of the whisky aroma profile based on headspace solid phase microextraction using different fibre coatings. J Chromatogr A. 2007; https://doi.org/10.1016/j.chroma.2006.09.014

8. Demyttenaere JCR, Sánchez Martinez JI, Verhé R, Sandra P, Kimpe N de. Analysis of volatiles of malt whisky by solid-phase microextraction and stir bar sorptive extraction. J Chromatogr A. 2003; https://doi.org/10.1016/S0021-9673(02)01471-1

9. Caldeira M, Rodrigues F, Perestrelo R, Marques JC, Câmara JS. Comparison of two extraction methods for evaluation of volatile constituents patterns in commercial whiskeys. Elucidation of the main odour-active compounds. Talanta. 2007; https://doi.org/10.1016/j.talanta.2007.05.029

10. Wanikawa A, Hosoi K, Takise I, Kato T. Detection or γ-Lactones in Malt Whisky. Journal of the Institute of Brewing. 2000; https://doi.org/10.1002/j.2050-0416.2000.tb00038.x

11. Buck N, Goblirsch T, Beauchamp J, Ortner E. Key Aroma Compounds in Two Bavarian Gins. Appl. Sci. 2020; https://doi.org/10.3390/app10207269

12. d'Acampora Zellner B, Dugo P, Dugo G, Mondello L. Gas chromatography-olfactometry in food flavour analysis. J Chromatogr A. 2008; https://doi.org/10.1016/j.chroma.2007.09.006

13. Haug H, Klein L, Sauerwald T, Poelke B, Beauchamp J, Roloff A. Sampling Volatile Organic Compound Emissions from Consumer Products: A Review. Crit Rev Anal Chem. 2022; https://doi.org/10.1080/10408347.2022.2136484

14. Rosso MC, Liberto E, Spigolon N, Fontana M, Somenzi M, Bicchi C, Cordero C. Evolution of potent odorants within the volatile metabolome of high-quality hazelnuts (Corylus avellana L.): evaluation by comprehensive two-dimensional gas chromatography coupled with mass spectrometry. Anal. Bioanal. Chem. 2018; https://doi.org/10.1007/s00216-017-0832-6

15. Liberto E, Bicchi C, Cagliero C, Cordero C, Rubiolo P, Sgorbini B. Headspace Sampling: An “Evergreen” Method in Constant Evolution to Characterize Food Flavors through their Volatile Fraction. In: Tranchida PQ, editor. Food Chemistry, Function and Analysis. Advanced Gas Chromatography in Food Analysis. Cambridge: The Royal Society of Chemistry; 2019. pp. 3–37.

16. Engel W, Bahr W, Schieberle P. Solvent assisted flavour evaporation - a new and versatile technique for the careful and direct isolation of aroma compounds from complex food matrices. Eur. Food Res. Technol. 1999; https://doi.org/10.1007/s002170050486

17. Nie Y, Kleine-Benne E. Determining Phenolic Compounds in Whisky using Direct Large Volume Injection and Stir Bar Sorptive Extraction. Gerstel AppNote 2/2012. 2012.

18. Nie Y, Kleine-Benne E. Using Three Types of Twister Phases for Stir Bar Sorptive Extraction of Whisky, Wine and Fruit Juice. Gerstel AppNote 3/2011. 2011.

19. Baltussen E, Sandra P, David F, Cramers C. Stir bar sorptive extraction (SBSE), a novel extraction technique for aqueous samples: Theory and principles. J. microcolumn sep. 1999; https://doi.org/10.1002/(SICI)1520-667X(1999)11:10<737:AID-MCS7>3.0.CO;2-4

20. Poisson L, Schieberle P. Characterization of the Key Aroma Compounds in an American Bourbon Whisky by Quantitative Measurements, Aroma Recombination, and Omission Studies. J. Agric. Food Chem. 2008; https://doi.org/10.1021/jf800383v

21. Vidal L, Ares G, Hedderley DI, Meyners M, Jaeger SR. Comparison of rate-all-that-apply (RATA) and check-all-that-apply (CATA) questions across seven consumer studies. Food Qual Prefer. 2018; https://doi.org/10.1016/j.foodqual.2016.12.013

22. Dehlholm C, Brockhoff PB, Meinert L, Aaslyng MD, Bredie WL. Rapid descriptive sensory methods – Comparison of Free Multiple Sorting, Partial Napping, Napping, Flash Profiling and conventional profiling. Food Qual Prefer. 2012; https://doi.org/10.1016/j.foodqual.2012.02.012

23. Pineau N, Girardi A, Lacoste Gregorutti C, Fillion L, Labbe D. Comparison of RATA, CATA, sorting and Napping® as rapid alternatives to sensory profiling in a food industry environment. Food Res Int. 2022; https://doi.org/10.1016/j.foodres.2022.111467

24. Zhang W, Liu T, Brown A, Ueland M, Forbes SL, Su SW. The Use of Electronic Nose for the Classification of Blended and Single Malt Scotch Whisky. IEEE Sensors Journal. 2022; https://doi.org/10.1109/JSEN.2022.3147185

25. González-Arjona D, López-Pérez G, González-Gallero V, González AG. Supervised pattern recognition procedures for discrimination of whiskeys from gas chromatography/mass spectrometry congener analysis. J. Agric. Food Chem. 2006; https://doi.org/10.1021/jf0517389

26. Zhu W, Benkwitz F, Kilmartin PA. Volatile-Based Prediction of Sauvignon Blanc Quality Gradings with Static Headspace-Gas Chromatography-Ion Mobility Spectrometry (SHS-GC-IMS) and Interpretable Machine Learning Techniques. J. Agric. Food Chem. 2021; https://doi.org/10.1021/acs.jafc.0c07899

27. Liu R-C, Li R, Wang Y, Jiang Z-T. Analysis of volatile odor compounds and aroma properties of European vinegar by the ultra-fast gas chromatographic electronic nose. J. Food Compos. Anal. 2022; https://doi.org/10.1016/j.jfca.2022.104673

28. Smyth H, Cozzolino D. Instrumental methods (spectroscopy, electronic nose, and tongue) as tools to predict taste and aroma in beverages: advantages and limitations. Chem Rev. 2013; https://doi.org/10.1021/cr300076c

29. Ribeiro JS, Augusto F, Salva TJG, Ferreira MMC. Prediction models for Arabica coffee beverage quality based on aroma analyses and chemometrics. Talanta. 2012; https://doi.org/10.1016/j.talanta.2012.09.022

30. Tao Y, Zhang L. Intensity prediction of typical aroma characters of cabernet sauvignon wine in Changli County (China). LWT. 2010; https://doi.org/10.1016/j.lwt.2010.06.003

31. Aznar M, López R, Cacho J, Ferreira V. Prediction of aged red wine aroma properties from aroma chemical composition. Partial least squares regression models. J. Agric. Food Chem. 2003; https://doi.org/10.1021/jf026115z

32. He C, Chen R, Ren K, Zhao G, He C, Hu B, Zou C, Jiang Y, Chen Y. A predictive model for the sensory aroma characteristics of flue-cured tobacco based on a back-propagation neural network. SN Appl. Sci. 2020; https://doi.org/10.1007/s42452-020-03656-4

33. Cano Marchal P, Sanmartin C, Satorres Martínez S, Gómez Ortega J, Mencarelli F, Gámez García J. Prediction of Fruity Aroma Intensity and Defect Presence in Virgin Olive Oil Using an Electronic Nose. Sensors. 2021; https://doi.org/10.3390/s21072298

34. Malfondet N, Brunerie P, Le Quéré J-L. Discrimination of French wine brandy origin by PTR-MS headspace analysis using ethanol ionization and sensory assessment. Anal. Bioanal. Chem. 2021; https://doi.org/10.1007/s00216-021-03275-x

35. Grasskamp AT, Singh S, Haug H, Sauerwald T. Assisting the automated analysis of chemical-analytical measurements in spirits using validated algorithms and an intuitive user interface (manuscript submitted). JSSS. 2022.

36. Haug H, Singh S, Grasskamp A, Sauerwald T. P5.1 - Automatisierte Auswertung chromatographischer Daten für die Bewertung von Whisky. In: AMA Association for Sensors + Measurement, editor. Tagungsband zum 15. Dresdner Sensorsymposium; 2021. pp. 245–250.

37. Grasskamp AT, Singh S, Haug H, Sauerwald T. Unterstützung der automatisierten Auswertung chemisch-analytischer Messungen von Spirituosen durch validierte Algorithmen und eine intuitive Benutzeroberfläche. In: Tagungsband Sensoren und Messsysteme. Berlin Offenbach: VDE Verlag GmbH; 2022. pp. 487–491.

38. Ares G, Bruzzone F, Vidal L, Cadena RS, Giménez A, Pineau B, Hunter DC, Paisley AG, Jaeger SR. Evaluation of a rating-based variant of check-all-that-apply questions: Rate-all-that-apply (RATA). Food Qual Prefer. 2014; https://doi.org/10.1016/j.foodqual.2014.03.006

39. van den Dool H, Kratz PD. A generalization of the retention index system including linear temperature programmed gas—liquid partition chromatography. J Chromatogr A. 1963; https://doi.org/10.1016/S0021-9673(01)80947-X

40. Biller JE, Biemann K. Reconstructed Mass Spectra, A Novel Approach for the Utilization of Gas Chromatograph—Mass Spectrometer Data. Anal. Lett. 1974; https://doi.org/10.1080/00032717408058783

41. d'Acampora Zellner B, Bicchi C, Dugo P, Rubiolo P, Dugo G, Mondello L. Linear retention indices in gas chromatographic analysis: a review. Flavour Fragr J. 2008; https://doi.org/10.1002/ffj.1887

42. Virtanen P, Gommers R, Oliphant TE, Haberland M, Reddy T, Cournapeau D, Burovski E, Peterson P, Weckesser W, Bright J, van der Walt SJ, Brett M, Wilson J, Millman KJ, Mayorov N, Nelson ARJ, Jones E, Kern R, Larson E, Carey CJ, Polat İ, Feng Y, Moore EW, VanderPlas J, Laxalde D, Perktold J, Cimrman R, Henriksen I, Quintero EA, Harris CR, Archibald AM, Ribeiro AH, Pedregosa F, van Mulbregt P. SciPy 1.0: fundamental algorithms for scientific computing in Python. Nat Methods. 2020; https://doi.org/10.1038/s41592-019-0686-2

43. Stein SE, Scott DR. Optimization and testing of mass spectral library search algorithms for compound identification. J. Am. Soc. Mass Spectrom. 1994; https://doi.org/10.1016/1044-0305(94)87009-8

44. PubChem. Guaiacol. National Library of Medicine. https://pubchem.ncbi.nlm.nih.gov/compound/460. Accessed 18 Nov 2022.

45. Mall V, Schieberle P. Decoding the Unique Peaty Aroma of Islay Scotch Single Malt Whisky by Means of the Sensomics Concept. In: Siegmund B, Leitner E, editors. Flavour Science: Proceedings of the XV Weurman Flavour Reseach Symposium. Graz: Verlag der Technischen Universität Graz; 2018. pp. 83–86.

46. Ghadiriasli R, Wagenstaller M, Buettner A. Identification of odorous compounds in oak wood using odor extract dilution analysis and two-dimensional gas chromatography-mass spectrometry/olfactometry. Anal. Bioanal. Chem. 2018; https://doi.org/10.1007/s00216-018-1264-7

47. Wiedmer C, Velasco-Schön C, Buettner A. Characterization of odorants in inflatable aquatic toys and swimming learning devices—which substances are causative for the characteristic odor and potentially harmful? Anal. Bioanal. Chem. 2017; https://doi.org/10.1007/s00216-017-0330-x

48. Bax C, Sironi S, Capelli L. How Can Odors Be Measured? An Overview of Methods and Their Applications. Atmosphere. 2020; https://doi.org/10.3390/atmos11010092

49. Stupak M, Goodall I, Tomaniova M, Pulkrabova J, Hajslova J. A novel approach to assess the quality and authenticity of Scotch Whisky based on gas chromatography coupled to high resolution mass spectrometry. Anal. Chim. Acta. 2018; https://doi.org/10.1016/j.aca.2018.09.017

50. Wiśniewska P, Boqué R, Borràs E, Busto O, Wardencki W, Namieśnik J, Dymerski T. Authentication of whisky due to its botanical origin and way of production by instrumental analysis and multivariate classification methods. Spectrochim Acta A Mol Biomol Spectrosc. 2017; https://doi.org/10.1016/j.saa.2016.10.042

51. Liu A, Zhang H, Liu T, Gong P, Wang Y, Wang H, Tian X, Liu Q, Cui Q, Xie X, Zhang L, Yi H. Aroma classification and flavor characterization of Streptococcus thermophilus fermented milk by HS-GC-IMS and HS-SPME-GC-TOF/MS. Food Biosci. 2022; https://doi.org/10.1016/j.fbio.2022.101832

52. Bi K, Zhang D, Qiu T, Huang Y. GC-MS Fingerprints Profiling Using Machine Learning Models for Food Flavor Prediction. Processes. 2019; https://doi.org/10.3390/pr8010023

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