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1 **Chemometric Modeling Of Coffee Sensory Notes Through Their Chemical Signatures:**
2 **Potential And Limits In Defining An Analytical Tool For Quality Control**

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23 **ABSTRACT**

24 Aroma is a primary hedonic aspect of a good coffee. Coffee aroma quality is generally defined by
25 cup tasting, which however is time-consuming in terms of panel training and alignment, and too
26 subjective. It is challenging to define a relationship between chemical profile and aroma sensory
27 impact, but it might provide an objective evaluation of industrial products. This study aimed to define
28 the chemical signature of coffee sensory notes, to develop prediction models based on analytical
29 measurements for use at the control level. In particular, the sensory profile was linked with the
30 chemical composition defined by HS-SPME-GC-MS, using a chemometric-driven approach. The
31 strategy was found to be discriminative and informative, identifying aroma compounds characteristic
32 of the selected sensory notes. The predictive ability in defining the sensory scores of each aroma note
33 was used as a validation tool for the chemical signatures characterized. The most reliable models
34 were those obtained for woody, bitter, and acidic properties, whose selected volatiles reliably
35 represented the sensory note fingerprints. Prediction models could be exploited in quality control, but
36 compromises must be determined if they are to become complementary to panel tasting.

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43 *Keywords: coffee aroma, sensory note fingerprints, HS-SPME-GC-MS, chemometrics*

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46 INTRODUCTION

47 Coffee aroma and flavor are the most important properties determining consumers' preference and
48 acceptance and, together with price, are the main aspects underlying a coffee's commercial success.¹⁻

49 ³ Coffee companies must evaluate the quality of the beans they aim to buy, to determine the best
50 coffees to use in their blends, and/or which coffees are of sufficiently high quality to be marketed as
51 "single origin". Several attributes are considered in qualifying a good coffee, including lack of
52 defects, bean color and size, and flavor, the latter aspect being recognized as indispensable. Cupping
53 protocols are international standards for cupping and grading coffees as a function of their sensory
54 properties.^{4,5}

55 However, sensory methods are expensive and time-consuming in terms of panel training and
56 alignment, and sometimes not sufficiently precise for a critical and objective evaluation; they are also
57 rather difficult to apply at-line for immediate feedback. The sensory approach adopted to date has
58 been quantitative descriptive analysis, with studies at the molecular level to disclose relationships
59 between chemical composition and sensory response. The sensory lexicon related to coffee is a
60 descriptive tool used worldwide to define aroma and flavor attributes quantitatively, through scaled
61 scores. The lexicon used when measuring the sensory aspects of different flavor attributes is therefore
62 of great importance, and must carefully be defined when comparing chemical and sensory data,
63 because non-specific language may create confusion. This approach has successfully been used by
64 trained professionals to evaluate coffee, enabling different panels to obtain the same intensity score
65 for each attribute for a given sample.⁶⁻⁸ However, well-designed and standardized chemo-sensory
66 evaluation is the key point to identify the chemicals responsible for a given sensorial note. The
67 definition of a relationship between chemical profile and aroma sensory impact is thus an important
68 challenge in both the analytical and the industrial fields, because it may enable food industries to
69 obtain a further objective evaluation, independent of or complementary to the panel's subjectivity, of
70 their products.

71 Gas-chromatography combined with mass-spectrometry (GC-MS) is the analytical technique of
72 election to study the composition of coffee aroma.⁹⁻¹² Conversely, several different sampling
73 approaches have been used to extract and concentrate flavor components, and more particularly
74 volatile compounds, directly from ground coffee (powder) and/or from the coffee brew. Sample
75 preparation is the crucial step in any analytical procedure, and must enable the recovery of chemical
76 components representative of each sensory informative note.^{1,13-24} Furthermore, in quality control,
77 the entire analytical procedure used to study chemicals related to the sensory experience should be
78 integrated and fully automated. In this context, chemometrics acts as a bridge linking sensory
79 properties to the chemical information underlying them; it can be used in quality assurance and
80 control, in product/blend development, in benchmarking new products and evaluating their probable
81 market impact, and in predicting preferences based on formulation changes.^{25,26} Furthermore,
82 chemometrics can provide information about the chemicals that discriminate among sensory
83 attributes, and link those chemicals to sensory perception through correlation models. The
84 conventional strategy in aroma studies implies that a single odorant is considered together with its
85 sensory description. Conversely, correlation through chemometrics makes it possible: to
86 simultaneously measure all compounds eliciting a peculiar sensory perception, and to link the quali-
87 quantitative distribution of odorants and their mutual and cross-modal interactions to the odor
88 perceived, through the sensory scores provided by the panel.^{13,21,27-29} However, reliable models that
89 describe a sensory note representative of the variability of coffee require: a large number of different
90 coffee samples, and fast analytical techniques applicable at-line or on-line, as a complement to the
91 verdict of the sensory panel. Several studies have addressed the sensory-instrumental relationship
92 relating to the sensory properties of coffee, but most looked at correlations among small and uniform
93 pools of samples, without taking into account the wide variability of coffees caused by origin, post-
94 harvest processing, and roasting.^{21,30,31}

95 This study is part of a wider project aiming to correlate the sensory characteristics of coffee aroma
96 with its chemical composition, in order to provide an objective tool that is complementary to sensory
97 evaluation, and that can be applied for routine use.

98 This part of the study, in particular, focuses on the use of chemometrics as a tool to define the odorants
99 characterizing the chemical signature of different coffee aroma notes, and to validate it for sensory
100 score prediction (Figure 1). Coffee samples with particular sensory characteristics were included as
101 representative of commercial coffees; samples were of different origins, species, and submitted to
102 different post-harvest treatments, as occurs in quality control at the industrial level upon acceptance
103 of incoming beans. Specimens were analyzed both sensorially and for their volatiles composition.
104 Sensory evaluation was done by an expert coffee-cupping panel, through a quantitative descriptive
105 analysis using a monadic approach. Sensory attributes included acidity, bitterness, woody, fruity,
106 flowery, spicy, and nutty notes, aroma intensity, body, and astringency. Chemical analyses were
107 carried out by headspace solid-phase micro-extraction combined with gas chromatography mass
108 spectrometry (HS-SPME-GC-MS). This combination may also be included within automatic Total
109 Analysis Systems (TAS), with which a large number of samples can be screened for quality control
110 of in-cup coffee sensory quality.^{9,32,33} The demand for sensory quality control and evaluation is
111 becoming crucial for coffee producers; the choice of this TAS method aimed to reconcile the need
112 for full characterization with that of screening increasingly large numbers of samples. The choice of
113 analytical strategy was driven by the need to balance these two requirements, but was also responsible
114 for the strategy's potentials and limits.

115

116 **Materials and Methods**

117 ***Reagents and Matrices***

118 Lavazza S.p.A. (Turin, Italy) kindly supplied coffee samples, consisting of roasted ground coffee
119 suitable for a coffee-filter machine, over a period of 15 months.

120 156 coffee samples with distinctive sensory notes, originating from different countries (Ethiopia,
121 Papua New Guinea, Colombia, Brazil, India, Indonesia, Tanzania, Uganda, and Vietnam), of the
122 species *Coffea arabica* L. (Arabica) and *Coffea canephora* Pierre (Robusta), were analyzed in
123 replicates. Table 1 lists twenty samples with their sensorial characterization. Samples 1-8 (five
124 replicates each, $n=40$) were used during the first part of the study to determine the most suitable
125 sample preparation method to study the relationship between chemical and sensory attributes.³⁴
126 Samples 9 to 20 (three replicates each, $n=36$) were a selection of samples specifically characterized
127 by woody and bitter notes, with scores at the two extremes (highest-lowest) of a 0-10 scale; these are
128 also indicated in the text as “stressed samples”. The roasting degree of each sample was carefully
129 measured by ground bean light reflectance, with a single-beam Color Test 2 instrument Neuhaus
130 Neotec (Genderkese, Germany) at a wavelength of 900 nm, on 25-30 g of ground coffee. Roasting
131 degree was set at 55° Nh, to be close to the international standardization protocol for cupping.⁵
132 Samples were roasted within 24 h prior to cupping, and left for at least 8h to stabilize. For clarity,
133 samples are labeled in the text with their origins.

134 Pure reference standards for identity confirmation were from Sigma-Aldrich (Milan, Italy): table, and
135 *n*-alkanes (n-C9 to n-C25) for Linear Retention Index (LRI) determination.

136 Internal standards (ISTDs) for analyte response normalization were *n*-C₁₃. A standard stock solution
137 of ISTDs at 1000 mg/L was prepared in dibutylphtalate (Sigma-Aldrich, Milan, Italy) and stored in
138 a sealed vial at -18 °C.

139

140 ***Headspace solid phase microextraction (HS-SPME) sampling***

141 The fiber was 1 cm length, coated with a polydimethylsiloxane/pivinybenzene (PDMS/DVB), 65
142 μm, conditioned before use as recommended by the manufacturer. The SPME device was from
143 Supelco (Bellfonte, PA). Coffee aroma compounds were sampled by automated headspace solid
144 phase microextraction (auto-HS-SPME), using a Combi-PAL AOC 5000 (Shimadzu, Milan, Italy),

145 assembled in-line with a Shimadzu QP2010 GC–MS system, controlled by Shimadzu GC–MS
146 Solution 2.51 software (Shimadzu, Milan, Italy).

147 *HS-SPME of the coffee powder*: 1.500 ± 0.010 g of powder were weighed in a septum-sealed gas vial
148 (20 mL); the resulting headspace was sampled through the PDMS/DVB SPME fiber for 40 min at 50
149 °C at a stirring speed of 350 rpm. The internal standard had previously been loaded onto the fiber³⁵
150 by sampling 5µL of a 1000 mg/L solution of *n*-C₁₃ in dibutylphthalate in a 20mL headspace vial for
151 20 min at 50 °C, stirring speed 350 rpm. After sampling, the accumulated analytes were recovered by
152 thermal desorption of the fiber for 5 min at 250 °C into the GC injector, and then transferred on-line
153 to the gas-chromatographic column. All samples were analyzed in duplicate.

154

155 ***GC-MS analysis conditions***

156 *GC-MS analysis - Chromatographic conditions*: injector temperature: 250 °C, injection mode:
157 splitless; carrier gas: helium, flow rate: 1 mL/min; fiber desorption and reconditioning times: 5 min;
158 column: SGE SolGelwax (100% polyethylene glycol) 300 mm x 0.25 mm i.d., 0.25 µm (SGE-
159 Melbourne, Australia). Temperature program, from 40 °C (1 min) to 200 °C at 3 °C/min and to 250
160 °C at 10 °C/min (5 min).

161 *MSD conditions*: ionization mode: EI (70 eV), temperatures: ion source: 200 °C; quadrupole: 150 °C;
162 transfer line: 250 °C; scan range: *m/z* 35-350.

163

164 ***Identification of volatile components***. Aroma compounds sampled from the headspace of the coffee
165 powder were identified through their linear retention indices (LRI)^{36,37} and EI-MS spectra, compared
166 to those of authentic standards or, tentatively, to those collected in-house or in commercial libraries
167 (Wiley 7N and Nist 05 ver 2.0 Mass Spectral Data).

168

169 ***Descriptive sensory analysis of coffee aroma***

170 The samples were submitted to sensory evaluation through quantitative descriptive analysis (QDA)
171 by the Lavazza trained panel of experts in coffee evaluation, following the SCAA Q cupping and
172 grading protocol.^{4,5,38} This protocol entails three tasting steps, after roasting to a set color (55-60 °Nh)
173 and eight hours of sample stabilization: i) evaluation of the aroma by sniffing the dry ground coffee,
174 ii) evaluation of the aroma by sniffing the brew 3 minutes after its preparation and stirring, and iii)
175 flavor evaluation after 8-10 min. The attributes aftertaste, acidity, body, and balance are evaluated by
176 tasting the brew, spraying it into the mouth to maximize retro-nasal vapors.

177 In the preliminary part of the study, five panelists determined the notes to be considered: flavor and
178 body (mouthfeel), astringency, and aroma intensity. In the second part, ten panelists assessed cup
179 quality for flowery, fruity, woody, nutty, spicy, acidity, and bitterness. The quality and intensity of
180 each attribute were evaluated simultaneously, upon a scale from 0 to 10. ANOVA analysis was run
181 to verify panel alignment on each attribute. Average scores from experts whose evaluations were
182 similar were used as “main scores” for the attributes under investigation.

183

184 ***Data processing***

185 Chromatographic data were collected using Shimadzu GCMS Solution 2.5SU1 software(Shimadzu).
186 Principal Component Analysis (PCA) was used to detect sample groups and outlier(s) within
187 chemical and sensory data. Partial Least Square Discriminant Analysis (PLS-DA) was then performed
188 on the sensory scaled samples (low-high score range) to identify the compounds most closely related
189 to a sensory attribute, and Partial Least Square Regression (PLS) was used to correlate chemicals to
190 sensory attributes, and to evaluate the ability of extracted chemical variables to predict sensory scores.
191 HS-SPME-GC-MS profiles normalized to ISTD were used (i.e. analytes target ion areas *versus* the
192 internal standard target ion area). Auto-scaling was applied as data pretreatment: this step ensured
193 that the contribution of each X variable (odorant) to the Y variable (sensory score) was unbiased.
194 One-way ANOVA and t-test on the sensorial results, and PCA, PLS-DA, and PLS, were run by
195 XLSTAT software (Addinsoft, Paris, France).

196

197 **RESULTS AND DISCUSSION**

198 *Qualitative descriptive profiles*

199 PCA is relevant in chemometrics mainly as a standard tool to display the qualitative aroma profiles
200 of samples. In QDA, a panel of trained assessors rates a number of samples for perceived intensities
201 of distinct attributes on scales; the panel follows reference protocols for specific food commodities
202 (e.g. coffee or olive oil), depending on the panel's experience and/or on the complexity of the matrix.
203 By averaging these intensity ratings and replicates, a data matrix may be built up, in which the rows
204 are food samples, and the columns the relative sensory attributes used to describe them^{25,26}. Analysis
205 of this data matrix by PCA can give information on both how coffee samples are related, and which
206 sensory notes best describe each sample. PCA was applied to the mean QDA sensory scores for aroma
207 and flavor of eight samples, analyzed in five replicates by five panelists; the bi-plot of scores and
208 loadings are shown in (Figure 2). The PCs that accounted for 75.4% (PC1) and 14.4% (PC2) of the
209 total variance were extracted. Focusing on sensory attributes, aroma intensity dominated Robusta
210 samples (JAV, UGA INDO), and appeared to be correlated to spicy, woody, body, and bitter notes.
211 Acid and bitter are normal taste attributes; however, previous studies demonstrated that there were
212 correlations between volatiles and taste sensory attributes, since several volatiles and non-volatiles
213 have common reaction pathways during roasting.^{21,28,30}
214 Moreover, panelists perceive odors via ortho- and retro-nasal pathways. This is the result both of
215 compound mutual interactions and of cross-modal effects between odorants and taste, which can
216 amplify or modify perception that, physiologically, occurs in the brain. These interactions do not
217 occur at the molecular level.³⁹⁻⁴¹
218 Bitter notes were also closely related to nutty and astringent notes. In contrast, vectors for fruity,
219 flowery, and acid were different from those of the above descriptors, and were positively correlated
220 with Arabica samples (COL, PNG, INDIA, KAFA, BRA). Among these, the only exception is the

221 India sample (INDIA ARAB CHERRY) that shows sensory characteristics more similar to Robusta
222 samples.

223

224 ***From sensory evaluation to the related chemicals: a discriminative and informative guide***

225 A total of 95 compounds were identified (or tentatively identified). 17 compounds were unknown (or
226 not unequivocally identified) by HS-SPME-GC-MS in the coffee powder samples. Table 2 reports
227 the list of identified compounds with their Linear Retention Indices (LRIs). The coffee aroma
228 chemical profile of the first 40 samples obtained by HS-SPME-GC-MS was processed by PCA,
229 together with their sensory scores, to determine: whether groups and/or outliers were present, and the
230 relationship between samples and chemical-sensory variables. As expected, as well as sensory quality
231 analysis, PCA on the aroma chemical profile showed a discrimination ability, driven firstly by species
232 (Figure 3A), and then, within species, by the sensory characteristics peculiar to each origin (Figure 3
233 C, 3E). The Loadings Plot (Figure 3B) clearly showed that the sensory notes were split into two
234 groups: 1) the acid, flowery, fruity notes, which were located in the 1st quadrant of the Cartesian
235 plane, i.e. the location of the Arabica samples; 2) the bitter, nutty, woody, and spicy notes, lying in
236 the 3rd quadrant, i.e. the location of the Robusta samples. Several chemical variables described this
237 sample distribution, and thus these sensory notes (Figure 3B). Several pyrazines, (e.g. 2-*n*-
238 propylpyrazine, 2,6-diethylpyrazine, 2-methyl-3,5-diethylpyrazine, isopropenylpyrazine) and
239 phenolic derivatives, such as guaiacols, characterized the Robusta samples and were more closely
240 related to the roasty, tobacco, nutty, spicy, and woody notes, while furan derivatives, esters and
241 ketones were linked to the sweet, fruity, and floral sensory attributes.^{9,22,42}

242 Within the Robusta samples: a) JAVA was the most nutty sample, characterized by compound #48
243 (unk 4); b) UGA samples had high acidity and were chemically described by 2,3-butandione and 2,3-
244 pentandione, acetoxyacetone, hexanal, acetic acid, 1-hydroxy-2-butanone, and 1-*H*-pyrrole-2-
245 carboxaldehyde, compounds elicit musty, sour, pungent, buttery notes that can be related to acid
246 attributes; c) INDO was the most woody, spicy, and bitter sample, and was more full-bodied and

247 astringent, mostly characterized by several pyrazines and phenolic compounds, as mentioned above
248 (Figure 3D).

249 Within Arabica, separation between samples was achieved on PC1 and PC2: a) KAFAs were
250 characterized by high body, fruity note, and aroma intensity; chemical variables related to these
251 sensory attributes were furfuryl alcohol, methyl acetate, 5-methyl furfural, 2-cyclopenten-1-one-3
252 methyl, all of which are characterized by sweet, fruity, malty, and nutty notes; b) conversely, PNG
253 was mostly characterized by acetyl furan, 2-furfuryl-5-methylfuran, 2-furanmethanol propanoate, 2-
254 furfuryl furan (Figure 3F).

255 Although HS-SPME discriminates among analytes depending on their volatility/polarity, if used
256 under standardized conditions it provides reliable information for fingerprinting studies, and is
257 perfectly suitable for comparative analyses.⁴³ Although PCA applied to comprehensive sensory and
258 chemical data possesses great informative potential, it is difficult to define the chemical fingerprint
259 of a single, specific, note for the purpose of discriminating samples by their sensory characteristics.
260 It is therefore necessary to analyze the relationship between chemical compounds and sensory note
261 descriptions in greater depth, looking at the chemical variables most closely correlated with each
262 sensory note. Chemical variables showing a Pearson correlation coefficient above 0.5 (taken as cut-
263 off) were singled out to compare samples characterized by different sensory notes.

264 Table 2 reports the variables related to each sensory attribute (except for aroma intensity, body, and
265 astringency). It may be seen that specific sensory notes (e.g. acid and flowery, or woody, bitter, nutty,
266 and spicy) are often described statistically by the same variables, i.e. the components statistically
267 correlated with these notes are very often the same. These results confirm that a specific sensory note
268 is described by component amounts and ratios, and rarely by single specific compounds.¹⁷

269 This may be due to the complexity of odor and taste perceptions, and to their mutual influence on the
270 actual perceived flavor. Interactions among odorants give odor synesthesia, while interactions
271 between odorants and tastants might give chemesthetic perception.^{2,3} Several examples of this

272 possible interaction are reported in Table 2; some note-related compounds were related statistically
273 to the note (X), although their odor description reported in the literature is different when considered
274 alone (X-L). For example, 2,3-Dimethylpyrazine alone has an odor description as nutty, and is also
275 related to other sensory attributes.³⁹

276 The percentage contribution of each compound to the whole chemical profile, correlated statistically
277 to a given sensory attribute, was monitored across all samples investigated. The percentage of each
278 compound was calculated considering their normalized responses (analytes target ion areas *versus*
279 the internal standard target ion area) within the whole targeted profile. Figure 4 shows a “heat map”
280 of the samples, scored on the normalized percentage contributions of components correlated with
281 woody, nutty, and “fresh” notes (acid, flowery/fruity). The slots in each row are colored according to
282 the magnitude of their values, from yellow (low percentage) to orange (high percentage). For instance,
283 in Figure 4A, guaiacol mainly contributes to the profiles of INDO, UGA and JAVA samples. INDO
284 samples had the highest contribution from variables related to woody. INDIA samples, despite being
285 Arabica, showed sensory characteristics similar to Robusta, thus confirming from the chemical
286 standpoint the sensory scores given by the panel (Table 1). Conversely, guaiacol, 1-*H*-pyrrole-2-
287 carboxaldehyde, (5*H*)-5-methyl-6,7-dihydrocyclopentanpyrazine, 2-furanmethanethiol, and
288 difurfuryldisulfide were directly involved in defining the woody note.^{17,19}

289 Not much may be deduced about the compounds linked to the fruity, acid, and flowery notes, because
290 of the similarity of the chemicals involved. However, the variables found to be correlated to these
291 notes agreed with the sensory scores of those samples (Table 1). For instance, fruity related
292 compounds, such as acetic acid and 3-methylbutanoic acid, were massively present in KAFA
293 samples, which achieved the highest score for the fruity note (Figure 4C).

294 It is difficult to determine which compound specifically contributes to a given note, and how it
295 contributes to it, for two reasons. The first is that the chemical definition of a sample’s sensory note
296 (i.e. its aroma signature) is linked to its composition, not only qualitatively but also quantitatively,

297 and, in particular, to the ratios between components. The second is the narrow range of the scores of
298 some notes, e.g. for nutty, from 0 to 3. When the range is narrow, seeking odorants that correlate to
299 the sensory note becomes challenging. To overcome these limitations, the range of sensory scores
300 must be maximized by selecting samples with “stressed” sensory notes, i.e. with high and low values.
301 This enables a more precise definition of the aroma compounds involved with the note, so as to verify
302 the method’s ability to correlate them with the sensory fingerprint.

303 A selection of “stressed” sensory samples representative of each note considered, independently of
304 species, origin, and post-harvest treatment, were analyzed and the chemical findings related to the
305 sensory scores (Table 1). “Stressed” samples means a panel selection of a new pool of samples with
306 considerable differences of sensory score within a given note.

307

308 ***Definition of note-related compounds (NRC) on representative “stressed” sensory samples***

309 A supervised chemometric tool (PLS-DA) was applied to study note-related compounds. PLS-DA
310 describes samples by calculating new variables that maximize separation between groups, while
311 minimizing variability within groups. Samples with the lowest score (for each target note) were
312 assigned to class 1, while those with the highest score were assigned to class 2. The impact of each
313 compound on the separation of the pool of samples into the two classes (1 and 2) was evaluated by
314 VIP (Variable Impact On Projections). The cut-off was arbitrarily chosen, for each note, as the point
315 at which the VIP values dropped sharply in the histogram. Some points emerged from this selection:
316 a) a single compound can contribute to the score of more than one sensory note. This was pointed out
317 above (non-supervised data elaboration) and was reported by Ribeiro et al.²⁸ in a study on prediction
318 models of the quality of Arabica coffee beverages;
319 b) the accuracy of variable selection is not the same for all notes. Variables selected to describe the
320 woody note were probably a consequence of clearer definition of the note (in terms both of maximized

321 scores and of panel alignment on the lexicon) across the group of samples, which led to more precise
322 identification of the most significant note-related compounds.

323

324 ***Validation of NRC in terms of sensory score prediction capability***

325 The compounds identified with PLS-DA for each sensory attribute were used to study the correlation
326 between chemical and sensory data on the whole data set, through a note-prediction model based on
327 the Partial Least Square Regression (PLS) algorithm. Samples were randomly divided into three
328 groups: a training set (131), a validation set (10), and a test set (15). Figure 5 shows the regression
329 parameters, curve and validation set fit for woody note, and score prediction on the external test
330 samples. The results showed correct sample distribution across the calibration interval, indicating the
331 model is reliable for sensory score prediction. Prediction reliability was evaluated through the
332 Standard Deviation Error in Calibration and in Prediction (SDEC and SDEP) from the predicted vs.
333 experimental scores, calculated as follows:

$$334 \text{ SDEC } (P) = \sqrt{\frac{\sum_{i=1}^n (y_i - \hat{y}_{i|t})^2}{n}}$$

335 Where:

336 y_i =experimental value, $\hat{y}_{i|t}$ = predicted value, n= number of observations.

337

338 The model showed close correlation between odorants selected and sensory scores. The predictive
339 ability was good, i.e. $Q^2=0.754$, with a SDEP=1.175.

340 Similar results, although not as good, were obtained for the other sensory attributes (Table 3). The
341 only exception was the nutty note, for which the model showed poor linearity ($R^2=0.467$), a wide
342 confidence limit (SDEC= 1.646) and very low predictive ability (SDEP= 1.426). This was chiefly

343 due to the difficulty over the lexicon used to define nutty and, as a consequence, to determine odorants
344 linked to it.

345 Although to differing extents, the results show good relationships between selected odorants and
346 sensory scores. Average standard error in score prediction was ± 1 , cross-validating the link between
347 the compounds selected and the sensory note description. From this perspective, the chemical
348 composition of woody and flowery notes was also investigated by sensomics.^{44,45} The preliminary
349 results of this inter-approach validation showed reasonable consistency between chemometrics and
350 sensomics for some of the target compounds. The compounds already confirmed by the sensomic
351 approach are listed in Figure 6.

352 The chemical structures of the volatiles identified as discriminant for the woody note are reported in
353 Figure 7A. Figure 7B reports the chemical structures of a selection of the volatiles derived from the
354 chemometric approach highly correlated (correlation coefficient >0.7) with those revealed by
355 sensomics. These chemical compounds (A and B) were used in the PLS model prediction of the
356 woody sensory scores. The chemometric-driven procedure can reveal the chemical aroma signature
357 of the sensory attributes investigated. At present, both performance and predictive ability of the
358 models are too closely related to the training set, and are also limited by its ability to cover the entire
359 range of scores of samples under study, i.e. woody vs. flowery. Compared to flowery, the robustness
360 of the woody note gives better prediction, thanks to two factors, namely the wide pool of samples,
361 covering the whole sensory score range; and the good panel alignment in woody note lexicon
362 recognition, providing a better estimation of an external test set.^{28-30,46}

363 Although this discussion has mainly focused on woody, nutty, and bitter notes, acid, spicy, and
364 flowery/fruity notes were also considered; they acted similarly to the notes discussed in depth,
365 including positive aspects and limitations.

366 The chemometric-driven approach was found to be discriminative, informative, and predictive in
367 revealing the chemical signature of the different coffee aroma notes. Discriminative, because it was

368 able to single out samples with peculiar aroma notes, independently of species, post-harvest
369 treatment, and origins. Informative, because it exploited the complementary and simultaneous use of
370 sensory and chemical data to define odorants able to describe the chemistry of aroma notes, stressing
371 the method's strengths and limitations. Predictive, because the panel-coherent sensory score
372 prediction, based on this chemometric approach, confirmed and reinforced the relevance and
373 significance of the volatiles selected by applying this procedure. Despite these positive results, the
374 final goal is still a distant one, because the models need of a sufficient number of samples to cover
375 the wide variability of samples (including seasonality); the accuracy in note definition and scoring
376 must be improved, chemometric data treatment can be optimized to better fit the dynamic range in
377 sensory evaluation. In any case, compromises must be made in applying a statistical model when
378 sensory attributes are all evaluated together.

379 The chemometric data-driven approach is promising for predicting sensory scores from chemical
380 data, and appears to provide a complementary tool that can contribute to objective sensory evaluation,
381 despite the great variability of coffee samples (origins, species, treatments, qualities) that are present
382 in the day-to-day situation in quality control at the industrial level.

383

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390

391 **Supporting information**

392 Table 1S The complete list of coffee samples analyzed in this study with their characteristics

393 This material is available free of charge via the internet at <http://pubs.acs.org>.

394

395

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- 506

507 **Figure captions**

508 Figure 1 Chemometric data treatment workflow in revealing the signature of the coffee aroma notes

509 Figure 2 Biplot of scores and factor loadings obtained by PCA for aroma descriptors of QDA for

510 coffees 1-8 ($n=40$). BRA: Brazil; COL: Colombia; JAV: Java; UGA: Uganda; PNG: Papua New

511 Guinea; INDO: Indonesia.

512 Figure 3 Scores and loading plots of the coffee samples obtained by chemical and sensory analysis,

513 A and B all samples, C and D Robusta, E and F Arabica coffees. BRA: □; COL: ◇; JAV: Δ; UGA: X;

514 PNG: * ; INDIA: ◻ ; INDO: ○ ; KAFA: +. For sample acronym see Table 1 and for loading

515 identification see Table 2.

516 Figure 4 Heat map of the percentage contribution of compounds correlated with: A) woody, B) nutty

517 and C) fresh notes (acid, flowery, fruity)

518 Figure 5 A) parameters used to build the model, B) regression curve and validation set fit for the

519 woody note, C) results of sensory score prediction on an external test samples

520 Figure 6 Compounds characterizing woody and flowery aroma notes confirmed by sensomics.

521 Figure 7 Chemical structures of the compounds highlighted by molecular sensory science as

522 important in the characterization of woody and used in the woody note chemometric prediction

523 model. (A) compounds shared between the two approaches (B) compounds derived from the

524 chemometric-driven approach as highly correlated (correlation coefficient >0.7) with those pointed

525 out by sensomics (Figure 6). Both (A) and (B) compounds were used in the PLS model prediction of

526 the woody sensory scores.

527

528 Table 1 Coffee samples and sensory characteristics. Species (A: Arabica, R: Robusta), Treatment (N: Natural, W: Washed).

| # | Sample acronym | Type | Species | Treatment | Acid | Bitter | Aroma intensity | Flowery | Fruity | Woody | Nutty | Spicy | Body | Astringency |
|---|----------------|--------------------|---------|-----------|------|--------|-----------------|---------|--------|-------|-------|-------|------|-------------|
| <i>SAMPLES WITH PECULIAR SENSORY ATTRIBUTES</i> | | | | | | | | | | | | | | |
| 1 | BRA | BRAZIL LA2 | A | N | 2 | 2 | 7 | 1 | 0 | 1 | 3 | 0 | 7 | 1 |
| 2 | COL | COLOMBIA CL1 | A | W | 4 | 1 | 8 | 3 | 3 | 0 | 0 | 0 | 7 | 1 |
| 3 | JAV | JAVA WB1 MB | R | W | 0 | 3 | 8 | 0 | 0 | 3 | 3 | 1 | 8 | 1 |
| 4 | UGA | UGANDA STD | R | N | 0 | 3 | 8 | 0 | 0 | 4 | 3 | 3 | 8 | 1 |
| 5 | PNG | PAPUA NG Y | A | W | 3 | 2 | 7 | 3 | 3 | 0 | 0 | 0 | 8 | 0 |
| 6 | INDIA | INDIA ARAB CHERRY | A | N | 2 | 4 | 8 | 0 | 0 | 2 | 2 | 3 | 8 | 1 |
| 7 | INDO | INDONESIA EK1 | R | N | 0 | 4 | 8 | 0 | 0 | 5 | 3 | 3 | 8 | 2 |
| 8 | KAFA | ETIOPIA KAFA GR. 3 | A | N | 4 | 1 | 8 | 3 | 6 | 0 | 0 | 0 | 7 | 0 |
| <i>SELECTED SENSORY STRESSED SAMPLES</i> | | | | | | | | | | | | | | |
| 9 | BRALA2 | BRAZIL LA2 | A | N | 4 | 1 | 6 | 0 | 0 | 0 | 5 | 0 | - | - |
| 10 | BRAGOU | BRAZIL GOURMET | A | N | 2 | 0 | 5 | 1 | 0 | 0 | 5 | 0 | - | - |
| 11 | JAV | JAVA MB | R | W | 1 | 2 | 7 | 0 | 0 | 1 | 7 | 0 | - | - |
| 12 | D2_65 | INDO_CN | R | N | 0 | 5 | 7 | 0 | 0 | 6 | 0 | 2 | - | - |

| | | | | | | | | | | | | | | |
|-----------|------------------|---------------|---|---|---|---|---|---|---|---|---|---|---|---|
| 13 | <i>D2_37</i> | BRASILE RFA | A | N | 3 | 0 | 8 | 0 | 0 | 0 | 8 | 0 | - | - |
| 14 | <i>D2_56</i> | Vietnam GR 2 | R | N | 0 | 4 | 8 | 0 | 0 | 7 | 1 | 1 | - | - |
| 15 | <i>INDOEK1</i> | INDONESIA EK1 | R | N | 0 | 4 | 8 | 0 | 0 | 7 | 1 | 3 | - | - |
| 16 | <i>INDIACHAB</i> | INDIA CHY AB | R | N | 0 | 3 | 7 | 0 | 0 | 7 | 3 | 6 | - | - |
| 17 | <i>BUK</i> | BUKOBA | R | N | 0 | 5 | 8 | 0 | 0 | 5 | 2 | 8 | - | - |
| 18 | <i>CON</i> | CONILON | R | N | 0 | 4 | 8 | 0 | 0 | 4 | 2 | 4 | - | - |
| 19 | <i>VIEGR2</i> | VIETNAM GR2 | R | N | 0 | 3 | 6 | 0 | 0 | 4 | 3 | 2 | - | - |
| 20 | <i>UGA</i> | UGANDA 18 UP | R | N | 0 | 4 | 8 | 0 | 0 | 6 | 1 | 7 | - | - |

529

Table 2 List of identified and *tentatively identified compounds.

| # | Compound Name | Odor Description ^{11,36,37} | Calc. LRI | Lit. LRI | Acid | Fruity | Flowery | Bitter | Nutty | Woody | Spicy |
|----|-----------------------|---|-----------|----------|------|--------|---------|--------|-------|-------|-------|
| 1 | Acetaldehyde | <i>Fruity</i> ¹¹ | 706 | 723 | | | | | | | |
| 2 | Acetone | <i>Ethereal, Apple, Pear</i> ³⁷ | 824 | 835 | | | | | | | |
| 3 | Methyl acetate | <i>Ethereal, Sweet, Fruit</i> ³⁷ | 828 | 839 | | | | | | | |
| 4 | 2-Methylfuran | <i>Chocolate, burnt, ethereal acetate</i> ¹¹ | 885 | 864 | | | | | | | |
| 5 | 2-Butanone | <i>Ethereal</i> ³⁷ | 906 | 905 | | | | | | | |
| 6 | 2-Methylbutanal | <i>Chocolate</i> ¹¹ | 914 | 931 | | | | | | | |
| 7 | 3-Methylbutanal | <i>Malty</i> ¹¹ | 918 | 936 | | | | | | | |
| 8 | 2,5-Dimethylfuran | <i>Ethereal</i> ³⁷ | 950 | 939 | | | | | | | |
| 9 | 2,3-Butanedione | <i>Buttery</i> ¹¹ | 978 | 963 | | | | | | | |
| 10 | 2,3-Pentanedione | <i>Buttery</i> ¹¹ | 1058 | 1060 | X | | X | | | | |
| 11 | 2-Vinylfuran | <i>Nutty, coffee</i> ³⁷ | 1071 | 1085 | | | | | | | |
| 12 | Hexanal | <i>Tallowy, leaf-like</i> ¹¹ | 1080 | 1098 | | | | | | | |
| 13 | 2,3-Hexanedione | <i>Buttery</i> ³⁷ | 1130 | 1110 | | | | | | | |
| 14 | 1-Methyl-1H-pyrrole | <i>Woody</i> ³⁷ | 1137 | 1140 | | | | | | | |
| 15 | 2-Vinyl-5-methylfuran | - | 1151 | 1152 | | | | | | | |
| 16 | Pyridine | <i>Fishy</i> ¹¹ | 1177 | 1177 | | | | | | | |
| 17 | Pyrazine | <i>Sweet, Floral</i> ³⁷ | 1209 | 1206 | | | | X | | | |
| 18 | Methylpyrazine | <i>Nutty</i> ³⁷ | 1262 | 1268 | | | | X | | | |
| 19 | 3-Hydroxy-2-butanone | <i>Buttery</i> ³⁷ | 1281 | 1285 | | | | | | | |
| 20 | 1-Hydroxy-2-propanone | <i>Sweet-Caramel-like</i> ³⁷ | 1297 | 1318 | X | | X | | | | |
| 21 | 2,5-Dimethylpyrazine | <i>Nutty-Roasted, Cocoa</i> ³⁷ | 1317 | 1321 | | | | X | | X | X |
| 22 | 2,6-Dimethylpyrazine | <i>Earthy-Chocolate</i> ³⁷ | 1324 | 1327 | | | | X | | X | X |
| 23 | Ethylpyrazine | <i>Nutty-roasted</i> ³⁷ | 1329 | 1343 | | | | X | X-L | X | X |
| 24 | 2,3-Dimethylpyrazine | <i>Nutty, coffee, peanut butter, walnut, caramel eather</i> ³⁷ | 1341 | 1354 | | | | X | X-L | X | X |
| 25 | 1-Hydroxy-2-butanone | <i>Sweet-caramel-like</i> ³⁶ | 1370 | 1381 | X | | X | | | | |

| # | Compound Name | Odor Description ^{11,36,37} | Calc. LRI | Lit. LRI | Acid | Fruity | Flowery | Bitter | Nutty | Woody | Spicy |
|----|---|---|-----------|----------|------|--------|---------|--------|-------|-------|-------|
| 26 | 3-Ethylpyridine | <i>Tobacco, caramel-like</i> ³⁷ | 1374 | 1384 | | | | X | | X | X |
| 27 | 2-Ethyl-5-methylpyrazine | <i>Coffee-like</i> ³⁷ | 1386 | 1399 | | | | X | X-L | X | X |
| 28 | 2-Ethyl-3-methylpyrazine+ Trimethylpyrazine | <i>Raw Potato</i> ³⁷ | 1399 | 1400 | | | | X-L | X | X | X |
| 29 | Unk 1(m/z: 54 [100%]; 43[78%]; 42[16.75%]) | - | 1405 | - | X | | X | | | | |
| 30 | 2- <i>n</i> -Propylpyrazine * | <i>Green vegetable</i> ¹¹ | 1413 | 1425 | | | | X | X | X | X-L |
| 31 | Unk 2(m/z: 112 [100%]; 68[73.76%]; 40[24.93%]) | - | 1418 | - | X | | X | | | | |
| 32 | 2-Furanmethanethiol | <i>Roasted, Burnt, coffee-like</i> ³⁷ | 1432 | 1440 | | | | X | X | X-L | X |
| 33 | 2-Ethyl-3,6-dimethylpyrazine | <i>Earthy, Baked</i> ¹¹ | 1441 | 1449 | | | | X-L | X | X | X |
| 34 | Acetic acid | <i>Sour, Pungent</i> ¹¹ | 1446 | 1454 | X-L | X | | | | | |
| 35 | 2,6-Diethylpyrazine | <i>Hazelnut-like</i> ³⁷ | 1457 | 1458 | | | | X | X-L | X | X |
| 36 | Furfural | <i>Sweet, Woody, Bready</i> ¹¹ | 1462 | 1467 | X | | X | | | | |
| 37 | Acetoxyacetone | <i>Fruity, Berry</i> ³⁷ | 1468 | 1467 | | | | | | | |
| 38 | Furfurylmethylsulfide | <i>Coffee-like odor</i> ³⁷ | 1483 | 1496 | | | | X-L | | X | X |
| 39 | 3,5-Diethyl-2-methylpyrazine | <i>Coffee-like</i> ³⁷ | 1489 | 1491 | | | | X | X | X | X |
| 40 | 2,5-Dimethyl-3(2 <i>H</i>)-furanone | <i>Caramel-like, fruity</i> ³⁷ | 1496 | 1490 | X | | X | | | | |
| 41 | Furfuryl formate | <i>Ethereal</i> ¹¹ | 1497 | 1497 | | | | | | | |
| 42 | Acetylfuran | <i>Sweet-caramel-like</i> ³⁷ | 1500 | 1498 | X | | X | | | | |
| 43 | 3-Methyl-2-Cyclopenten-1-one + 3,5-Diethyl-2-Methylpyrazine | <i>Burnt, Rubbery, earthy + coffee-like</i> ³⁷ | 1509 | 1509 | | | | X | X | X | X |
| 44 | 1- <i>H</i> -Pyrrole | <i>Sweet:ethereal</i> ¹¹ | 1513 | 1525 | | | | X | X | X | X-L |
| 45 | Benzaldehyde + 2-Methyl-3(2 <i>H</i>)-thiophenone *+ Furan-2-yl-propan-2-ol | <i>Sweet</i> ³⁷ | 1519 | 1520 | | | | | | | |
| 46 | 2-Oxopropylpropanoate | - | 1531 | 1531 | | | | | | | |
| 47 | Furfuryl acetate | <i>Garlic, pungent vegetable, onion</i> ¹¹ | 1538 | 1539 | | | | | | | |
| 48 | Unk 4(m/z: 110[100%]; 109[86.72%]; 53[50.99%]) | - | 1564 | - | | | | | | | |
| 49 | 5-Methyl Furfural | <i>Caramel-like</i> ³⁷ | 1570 | 1562 | X | | X | | | | |
| 50 | 2,3-Butandiole + 1-(5-Methyl-2-furyl)2-propanone | - | 1575 | 1582 | | | | | | | |
| 51 | 1-Methylethenylpyrazine | <i>Roasted, Nutty</i> ³⁶ | 1590 | - | | | | X | X-L | X | X |

| # | Compound Name | Odor Description ^{11,36,37} | Calc. LRI | Lit. LRI | Acid | Fruity | Flowery | Bitter | Nutty | Woody | Spicy |
|----|--|---|-----------|----------|------|--------|---------|--------|-------|-------|-------|
| 52 | Furfuryl propanoate | <i>Fruity</i> ³⁷ | 1598 | 1603 | | | | | | | |
| 53 | 2-Furfurylfuran | <i>Caramel-like, earthy, mushroom</i> ³⁷ | 1608 | - | | | | | | | X |
| 54 | (5H)-5-Methyl-6,7-dihydrocyclopentapyrazine | <i>Earthy</i> ³⁶ | 1611 | 1611 | | | | X-L | X | X | X |
| 55 | 1-Methylpyrrole-2-carboxaldehyde | <i>Cracked/pop-corn</i> ³⁷ | 1614 | 1635 | | | | | | | |
| 56 | 4-Hydroxybutanoate | - | 1621 | - | | | | | | | |
| 57 | Unk 6 (m/z: 137[100%]; 94[61.57%]; 122[37.71%]) | - | 1630 | - | | | | | | | |
| 58 | 2-Isopropenylpyrazine | <i>Caramel-like, Nutty</i> ³⁶ | 1633 | 1633 | | | | X | X-L | X | X |
| 59 | 2,5-Dihydro-3,5-dimethyl-2-furanone * | - | 1642 | 1640 | | | | | | | |
| 60 | 1-(1-methyl-1H-pyrrol-2-yl)-Ethanone * + 2-Acetyl-5-methyl pyrrole | - | 1649 | - | | | | | | | |
| 61 | Furfurylalcohol | <i>Mild, slightly caramel-like</i> ³⁷ | 1661 | 1664 | | | | | | | |
| 62 | 3-Methylbutanoic acid | <i>Acid, Herbaceous, Sour</i> ³⁷ | 1667 | 1670 | X-L | X-L | X-L | | | | |
| 63 | 3-Methyl-1,2-ciclohexanedione | <i>Saffron, burnt, chemical</i> ³⁷ | 1678 | - | | | | | | | |
| 64 | 2-Furfuryl-5-methylfuran | <i>Alliaceous, earthy, mushroom</i> ³⁷ | 1686 | 1636 | | | | | | | |
| 65 | 2-Acetyl-3-methylpyrazine* | <i>Nutty</i> ³⁶ | 1694 | 1719 | | | | X | X-L | X | X |
| 66 | Furfurylpentanoate | <i>Fruity</i> ³⁶ | 1702 | 1702 | | | | | | | |
| 67 | 2-Methyl-6-(1-propenyl)-pyrazine* | - | 1708 | 1719 | | | | X | X | X | X |
| 68 | Unk 11 (m/z:69[84-54%]; 41[100%];83 m/z[31.67%]) | - | 1709 | - | | | | | | | |
| 69 | 1-Acetyl-1,4-dihydropyridine* | - | 1716 | - | | | | X | | | |
| 70 | Unk 12 (m/z: 140[100%]; 43[55%]; 111[33.52%]) | - | 1726 | - | | | | | | | |
| 71 | Unk 13 (m/z: 54[100%]; 82[73.67%] ; 110 [57.91%]) | - | 1729 | - | | | | | | | |
| 72 | Unk 13b (m/z : 67 [100%]; 112[73.67%]; 53[55.59%]) | - | 1734 | - | | | | | | | |
| 73 | Unk 14 (m/z: 55; 84[48.75%]; 54[26.45%]) | - | 1745 | - | X | | X | | | | |
| 74 | Unk 15 (m/z: 119[100%]; 43[26.78%]; 64[25.39%]) | - | 1750 | - | | | | | | | |
| 75 | Methyl nicotinate + other | - | 1767 | 1778 | | | | X | | X | X |

| # | Compound Name | Odor Description ^{11,36,37} | Calc. LRI | Lit. LRI | Acid | Fruity | Flowery | Bitter | Nutty | Woody | Spicy |
|----|--|--|-----------|----------|------|--------|---------|--------|-------|-------|-------|
| 76 | Unk 17 (m/z: 95[100%]; 43[28.81%]; 138 [17.56%]) | - | 1772 | - | X | | X | | | | |
| 77 | Unk 18 (m/z: 123; 122[74.34%]; 126 [11.84%]) | - | 1777 | - | | | | | | | |
| 78 | 3-Methyl-2-butenic acid | <i>Phenolic</i> ³⁶ | 1786 | - | | | | | | | |
| 79 | Unk 20 (m/z:139; 43[12.25%]; 154[50.48%]) | - | 1791 | - | | | | X | | | |
| 80 | 2-Hydroxy-3-methyl-2-cyclopenten-1-one | <i>Caramel-like-Spicy</i> ³⁷ | 1820 | 1839 | | | | | | | |
| 81 | Furfurylpyrrole | <i>Green, hay-like</i> ³⁷ | 1853 | 1866 | | | | X | | X | X |
| 82 | Guaiacol | <i>Smoky/sweet</i> ¹¹ | 1860 | - | | | | X | | X | X-L |
| 83 | 2-Acetyl-5-methylfuran | <i>Caramel-like</i> ³⁷ | 1885 | - | X | | X | | | | |
| 84 | 3-Ethyl-2-hydroxy-2-Cyclopenten-1-one | <i>Caramel-like</i> ³⁷ | 1885 | - | | | | | | | |
| 85 | <i>trans</i> -Furfurylideneacetone* | - | 1897 | - | | | | | | | |
| 86 | Phenylethanol | <i>Floral, woody, honey-like</i> ³⁷ | 1902 | 1912 | | | | X | | X-L | X |
| 87 | Maltol | <i>Sweet, Caramel-like</i> ³⁷ | 1952 | 1960 | | | | | | | |
| 88 | 2-Acetylpyrrole | <i>Bitter, Roasted</i> ³⁷ | 1962 | 1971 | | | | X | | | X |
| 89 | Difurfurylether | <i>Coffee-like, mushroom</i> ³⁷ | 1980 | 1977 | | | | X | | | X |
| 90 | Phenol deriv* | - | 1997 | - | | | | X | | X | X |
| 91 | 1H-Pyrrole-2-carboxaldehyde | <i>Corny-Pungent</i> ³⁷ | 2012 | 2035 | | | | | | | |
| 92 | 4-Ethylguaiacol | <i>Spicy</i> ¹¹ | 2021 | 2037 | | | | X | | X | X-L |
| 93 | Nonanoic acid | <i>Nut-like, Fatty</i> ³⁷ | 2150 | 2159 | | | | | | | |
| 94 | 4-Vinylguaiacol | <i>Clove-like</i> ¹¹ | 2185 | 2193 | | | | X | | X-L | X-L |
| 95 | Difurfuryldisulfide | <i>Mushrooms, caramel-like</i> ³⁷ | 2536 | 2536 | | | | | | | |

Compounds with an “X” are related to each sensory note; “L” indicates that the compound alone directly elicits the peculiar note perception. Odor description is taken from literature references 11, 36, 37.

Table 3

Summary of the performances of sensory notes prediction models

| AROMA NOTE | R²_{LMO(10%)} | Q²_(10%) | SDEC | Q²_{(15%)EXT} | SDEP_{EXT} |
|-------------------|---|--------------------------------------|-------------|---|---------------------------|
| Woody | 0.816 | 0.659 | 0.977 | 0.754 | 1.175 |
| Bitter | 0.806 | 0.689 | 0.755 | 0.830 | 0.670 |
| Spicy | 0.684 | 0.298 | 1.337 | 0.653 | 1.155 |
| Acid | 0.831 | 0.497 | 1.019 | 0.734 | 0.890 |
| Fruity | 0.661 | 0.193 | 0.837 | 0.568 | 1.115 |
| Flowery | 0.793 | 0.342 | 1.047 | 0.475 | 1.244 |
| Nutty | 0.467 | 0.302 | 1.646 | 0.634 | 1.426 |

Figure 1

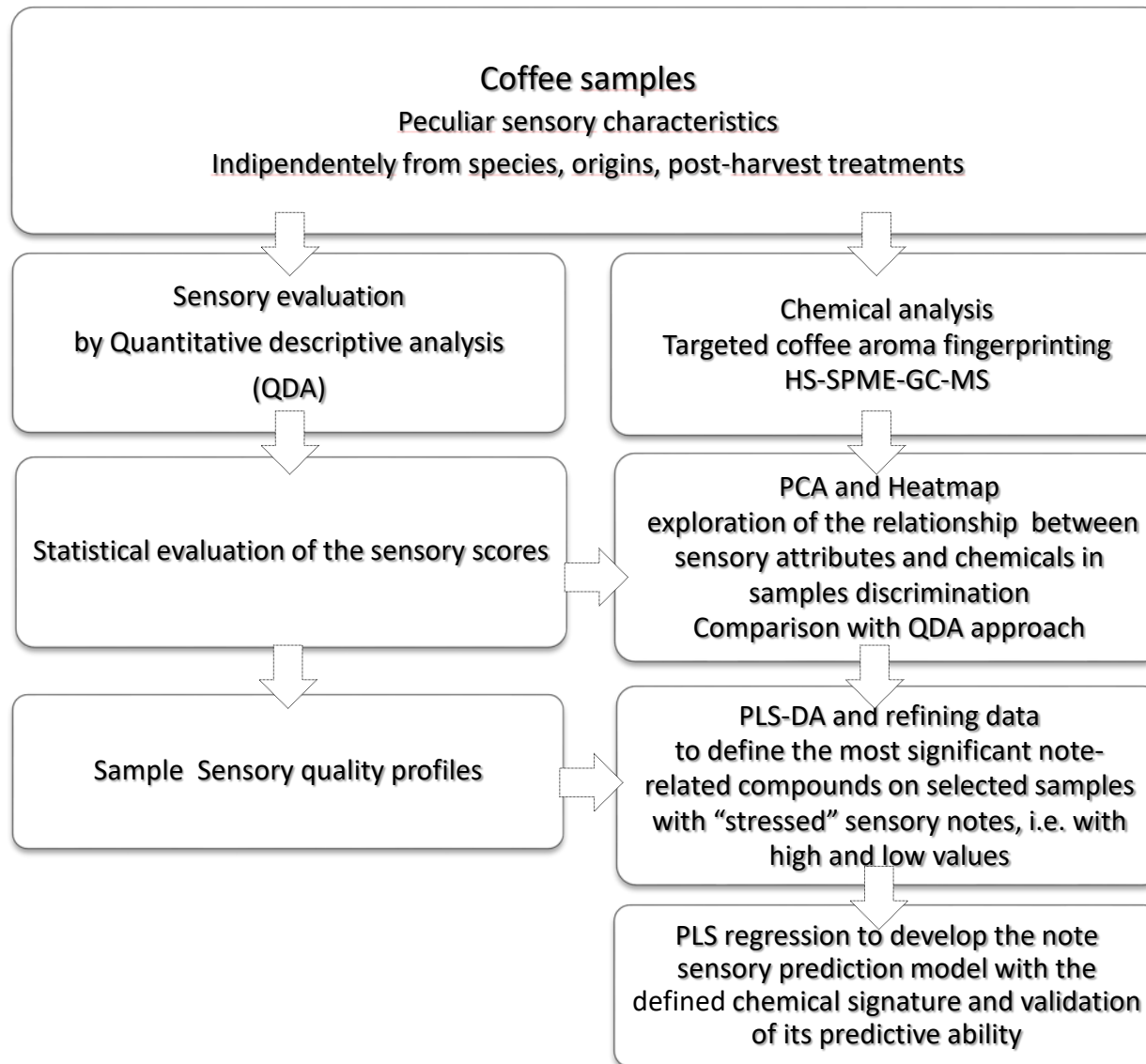


Figure 2

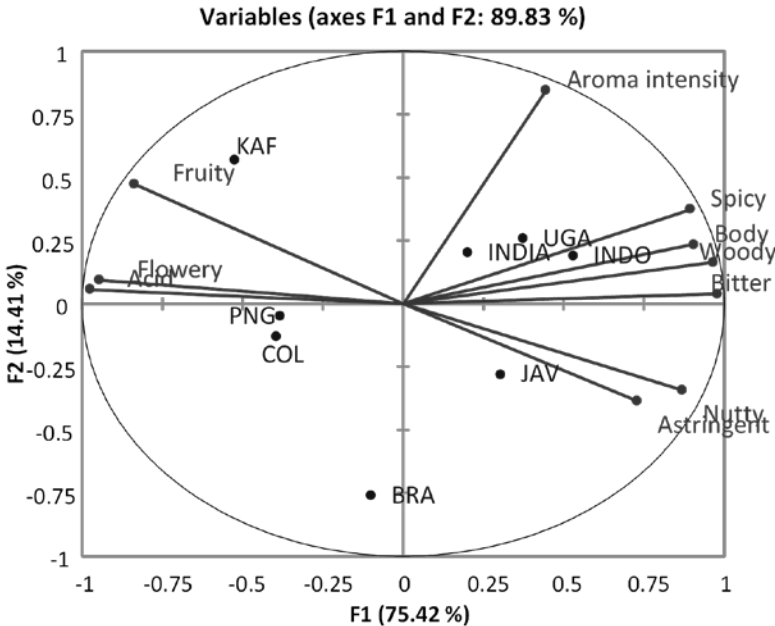


Figure 3

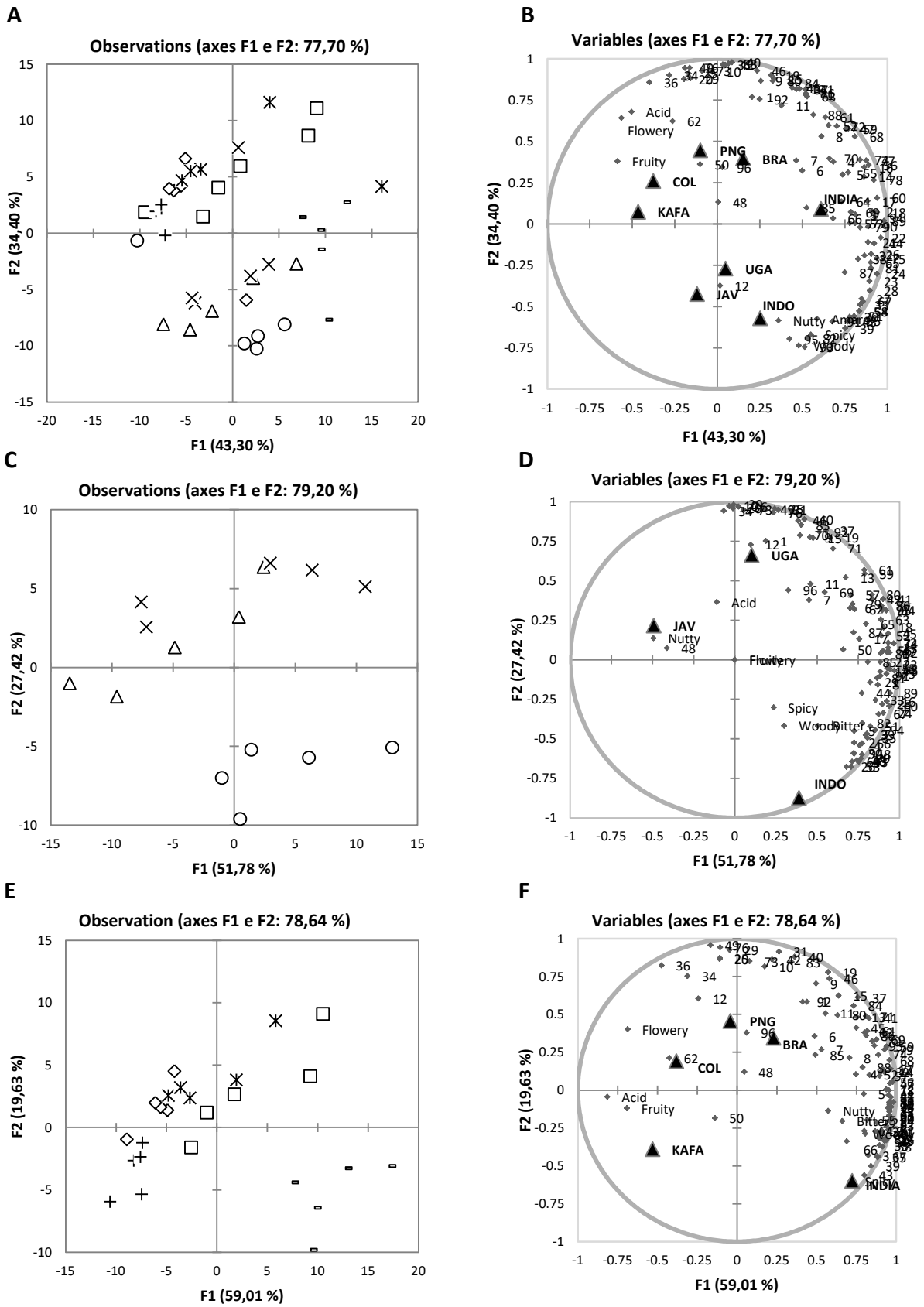


Figure 4

| A | WOODY | BRA | COL | JAV | UGA | PNG | INDIA | INDO | KAFA |
|---|-------------------------------|------------|------------|------------|------------|------------|--------------|-------------|-------------|
| 2,5-Dimethylpyrazine | | 2.867 | 2.665 | 3.638 | 3.402 | 2.539 | 3.521 | 3.980 | 3.453 |
| 2,6-Dimethylpyrazine | | 3.460 | 3.088 | 4.515 | 4.018 | 3.130 | 4.298 | 4.681 | 3.529 |
| Ethylpyrazine | | 1.437 | 1.208 | 2.220 | 1.957 | 1.216 | 1.779 | 2.192 | 1.353 |
| 2,3-Dimethylpyrazine | | 0.637 | 0.514 | 0.903 | 0.823 | 0.536 | 0.894 | 1.078 | 0.548 |
| 3-Ethylpyridine | | 0.121 | 0.081 | 0.119 | 0.132 | 0.101 | 0.198 | 0.229 | 0.100 |
| 2-Ethyl-5-methylpyrazine | | 1.260 | 1.121 | 2.230 | 1.888 | 1.095 | 1.781 | 2.256 | 1.370 |
| 2-Ethyl-3-methylpyrazine + trimethylpyrazine | | 1.589 | 1.346 | 2.640 | 2.270 | 1.359 | 2.458 | 2.979 | 1.568 |
| 2- <i>n</i> -Propylpyrazine | | 0.048 | 0.045 | 0.090 | 0.070 | 0.044 | 0.071 | 0.109 | 0.039 |
| 2-Furanmethanethiol | | 0.294 | 0.215 | 0.396 | 0.380 | 0.237 | 0.313 | 0.429 | 0.181 |
| 2-Ethyl-3,6-Dimethylpyrazine | | 0.907 | 0.753 | 1.840 | 1.500 | 0.659 | 1.649 | 1.991 | 0.659 |
| 2,6-Diethylpyrazine | | 0.348 | 0.286 | 0.726 | 0.597 | 0.296 | 0.619 | 0.898 | 0.356 |
| Furfurylmethylsulfide | | 0.172 | 0.192 | 0.204 | 0.239 | 0.220 | 0.301 | 0.425 | 0.196 |
| 3,5-Diethyl-2-methylpyrazine | | 0.152 | 0.124 | 0.391 | 0.312 | 0.134 | 0.324 | 0.454 | 0.174 |
| 3 Methyl-2-Cyclopenten-1-one + 3,5-Diethyl-2-Methylpyrazine | | 0.036 | 0.027 | 0.090 | 0.081 | 0.028 | 0.100 | 0.137 | 0.042 |
| 1 <i>H</i> -Pyrrole | | 0.544 | 0.345 | 0.643 | 0.572 | 0.397 | 0.646 | 0.693 | 0.332 |
| 1-Methylethenylpyrazine | | 0.148 | 0.122 | 0.278 | 0.224 | 0.124 | 0.209 | 0.318 | 0.134 |
| (5 <i>H</i>)-5-Methyl-6,7-Dihydrocyclopentapyrazine | | 0.204 | 0.173 | 0.374 | 0.326 | 0.183 | 0.321 | 0.456 | 0.188 |
| 1-Methylpyrrole-2-Carboxaldehyde | | 0.878 | 0.738 | 0.820 | 0.895 | 0.860 | 0.944 | 0.976 | 1.089 |
| 2-Isopropenylpyrazine | | 0.226 | 0.170 | 0.423 | 0.367 | 0.186 | 0.407 | 0.573 | 0.195 |
| 2-Acetyl-3-Methylpyrazine | | 0.373 | 0.314 | 0.560 | 0.461 | 0.315 | 0.454 | 0.504 | 0.343 |
| 2-Methyl-6-(1-propenyl)-pyrazine | | 0.184 | 0.149 | 0.355 | 0.289 | 0.149 | 0.337 | 0.405 | 0.179 |
| Methyl nicotinate +other | | 0.097 | 0.084 | 0.130 | 0.119 | 0.076 | 0.123 | 0.138 | 0.069 |
| Furfurylpyrrole | | 1.047 | 1.053 | 1.666 | 1.368 | 1.120 | 1.315 | 1.707 | 1.032 |
| Guaiaicol | | 0.382 | 0.416 | 1.010 | 1.556 | 0.479 | 0.739 | 2.023 | 0.442 |
| Benzeneethanol | | 0.159 | 0.104 | 0.143 | 0.319 | 0.132 | 0.192 | 0.270 | 0.095 |
| Phenol deriv | | 0.275 | 0.291 | 0.533 | 0.657 | 0.300 | 0.402 | 0.712 | 0.285 |
| 4-Ethyl-guaiaicol | | 0.319 | 0.302 | 1.188 | 1.251 | 0.302 | 0.610 | 2.220 | 0.173 |
| 4-Vinyl-guaiaicol | | 1.828 | 1.944 | 5.542 | 5.350 | 1.609 | 1.879 | 5.397 | 1.015 |
| | | | | | | | | | |
| | | | | | | | | | |
| B | NUTTY | BRA | COL | JAV | UGA | PNG | INDIA | INDO | KAFA |
| Ethylpyrazine | | 1.437 | 1.208 | 2.220 | 1.957 | 1.216 | 1.779 | 2.192 | 1.353 |
| 2,3-Dimethylpyrazine | | 0.637 | 0.514 | 0.903 | 0.823 | 0.536 | 0.894 | 1.078 | 0.548 |
| 2-Ethyl-5-methylpyrazine | | 1.260 | 1.121 | 2.230 | 1.888 | 1.095 | 1.781 | 2.256 | 1.370 |
| 2-Ethyl-3-methylpyrazine + Trimethylpyrazine | | 1.589 | 1.346 | 2.640 | 2.270 | 1.359 | 2.458 | 2.979 | 1.568 |
| 2- <i>n</i> -Propylpyrazine | | 0.048 | 0.045 | 0.090 | 0.070 | 0.044 | 0.071 | 0.109 | 0.039 |
| 2-Furanmethanethiol | | 0.294 | 0.215 | 0.396 | 0.380 | 0.237 | 0.313 | 0.429 | 0.181 |
| 2-Ethyl-3,6-dimethylpyrazine | | 0.907 | 0.753 | 1.840 | 1.500 | 0.659 | 1.649 | 1.991 | 0.659 |
| 2,6-Diethylpyrazine | | 0.348 | 0.286 | 0.726 | 0.597 | 0.296 | 0.619 | 0.898 | 0.356 |
| 3,5-Diethyl-2-methylpyrazine | | 0.152 | 0.124 | 0.391 | 0.312 | 0.134 | 0.324 | 0.454 | 0.174 |
| 3 Methyl-2-cyclopenten-1-one + 3,5-Diethyl-2-methylpyrazine | | 0.036 | 0.027 | 0.090 | 0.081 | 0.028 | 0.100 | 0.137 | 0.042 |
| 1 <i>H</i> -Pyrrole | | 0.544 | 0.345 | 0.643 | 0.572 | 0.397 | 0.646 | 0.693 | 0.332 |
| 1-Methylethenylpyrazine | | 0.148 | 0.122 | 0.278 | 0.224 | 0.124 | 0.209 | 0.318 | 0.134 |
| (5 <i>H</i>)-5-methyl-6,7-dihydrocyclopentapyrazine | | 0.204 | 0.173 | 0.374 | 0.326 | 0.183 | 0.321 | 0.456 | 0.188 |
| 2-Isopropenylpyrazine | | 0.226 | 0.170 | 0.423 | 0.367 | 0.186 | 0.407 | 0.573 | 0.195 |
| 2-Acetyl-3-methylpyrazine | | 0.373 | 0.314 | 0.560 | 0.461 | 0.315 | 0.454 | 0.504 | 0.343 |
| 2-Methyl-6-(1-propenyl)-pyrazine | | 0.184 | 0.149 | 0.355 | 0.289 | 0.149 | 0.337 | 0.405 | 0.179 |
| Methyl nicotinate +other | | 0.097 | 0.084 | 0.130 | 0.119 | 0.076 | 0.123 | 0.138 | 0.069 |
| Guaiaicol | | 0.382 | 0.416 | 1.010 | 1.556 | 0.479 | 0.739 | 2.023 | 0.442 |
| Benzenethanol | | 0.159 | 0.104 | 0.143 | 0.319 | 0.132 | 0.192 | 0.270 | 0.095 |
| Phenol deriv | | 0.275 | 0.291 | 0.533 | 0.657 | 0.300 | 0.402 | 0.712 | 0.285 |
| 4-Ethyl-guaiaicol | | 0.319 | 0.302 | 1.188 | 1.251 | 0.302 | 0.610 | 2.220 | 0.173 |
| 4-Vinyl-guaiaicol | | 1.828 | 1.944 | 5.542 | 5.350 | 1.609 | 1.879 | 5.397 | 1.015 |
| | | | | | | | | | |
| | | | | | | | | | |
| C | ACID/ FRUITY / FLOWERY | BRA | COL | JAV | UGA | PNG | INDIA | INDO | KAFA |
| 2,3-Pentanedione | | 0.299 | 0.337 | 0.189 | 0.184 | 0.346 | 0.190 | 0.094 | 0.314 |
| 1-Hydroxy-2-propanone | | 0.855 | 1.123 | 0.584 | 0.541 | 0.924 | 0.484 | 0.303 | 0.768 |
| 1-Hydroxy-2-butanone | | 0.077 | 0.098 | 0.044 | 0.048 | 0.080 | 0.042 | 0.027 | 0.071 |
| Unk 1 | | 0.379 | 0.447 | 0.246 | 0.241 | 0.375 | 0.177 | 0.110 | 0.329 |
| Unk 2 | | 0.132 | 0.143 | 0.090 | 0.100 | 0.140 | 0.089 | 0.059 | 0.138 |
| Acetic acid | | 4.783 | 7.639 | 3.544 | 3.163 | 7.246 | 3.826 | 2.041 | 6.848 |
| Furfural | | 3.243 | 5.369 | 2.003 | 2.334 | 4.131 | 1.600 | 1.020 | 4.023 |
| 2,5-Dimethyl-3(2 <i>H</i>)-Furanone | | 0.645 | 0.730 | 0.484 | 0.521 | 0.739 | 0.501 | 0.357 | 0.739 |
| Acetyl furan | | 1.393 | 1.892 | 0.926 | 1.104 | 1.814 | 1.202 | 0.990 | 1.784 |
| 5-Methyl Furfural | | 6.024 | 7.797 | 4.483 | 5.187 | 7.154 | 3.995 | 2.880 | 7.350 |
| 3-Methylbutanoic acid | | 2.346 | 3.072 | 2.140 | 2.713 | 3.533 | 2.032 | 2.412 | 5.151 |
| Unk 14 | | 0.263 | 0.327 | 0.192 | 0.173 | 0.299 | 0.189 | 0.123 | 0.273 |
| Unk 17 | | 0.338 | 0.471 | 0.258 | 0.293 | 0.430 | 0.241 | 0.182 | 0.419 |
| Unk 21 | | 0.826 | 1.032 | 0.563 | 0.671 | 1.068 | 0.696 | 0.412 | 0.937 |

Figure 5

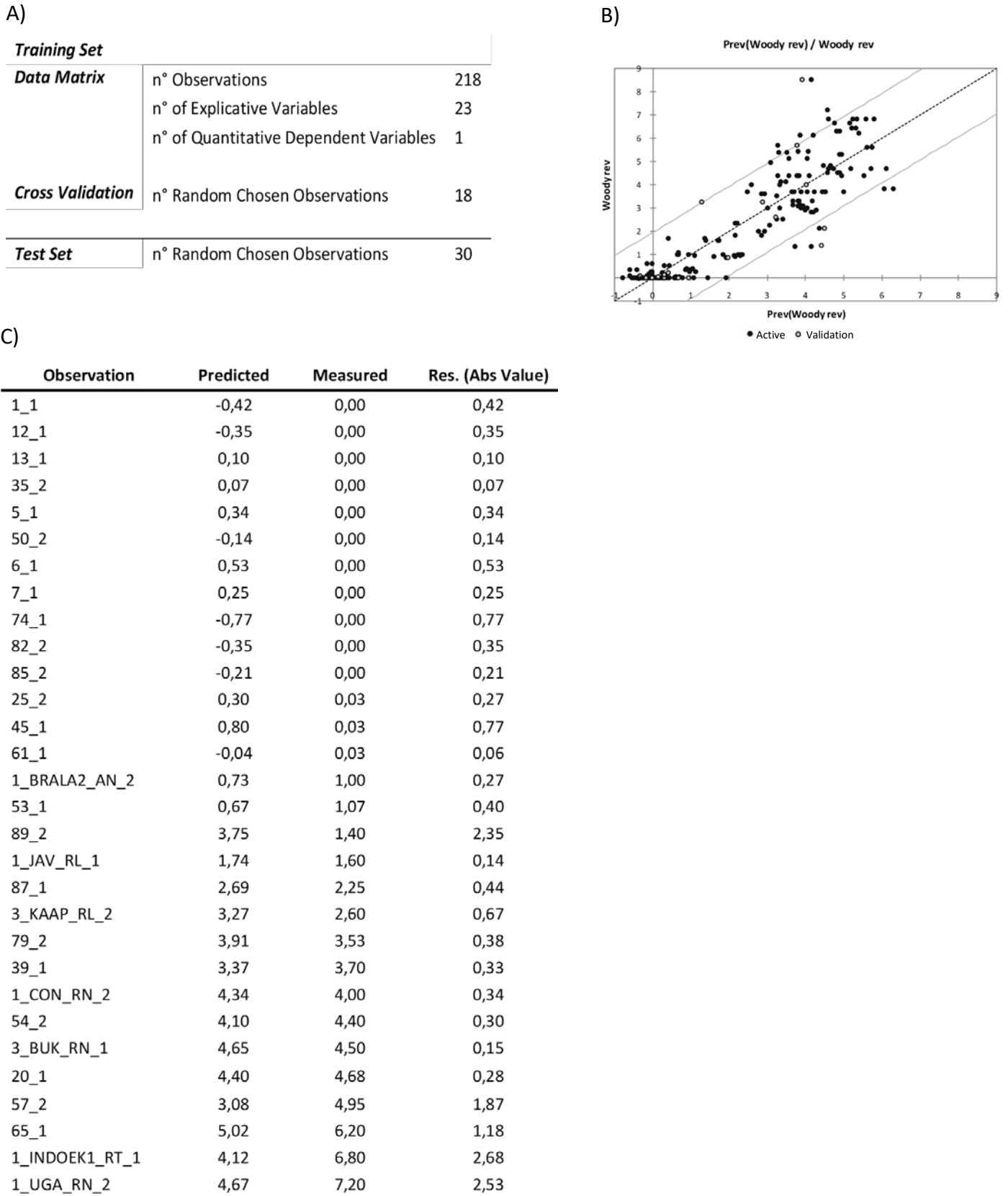


Figure 6

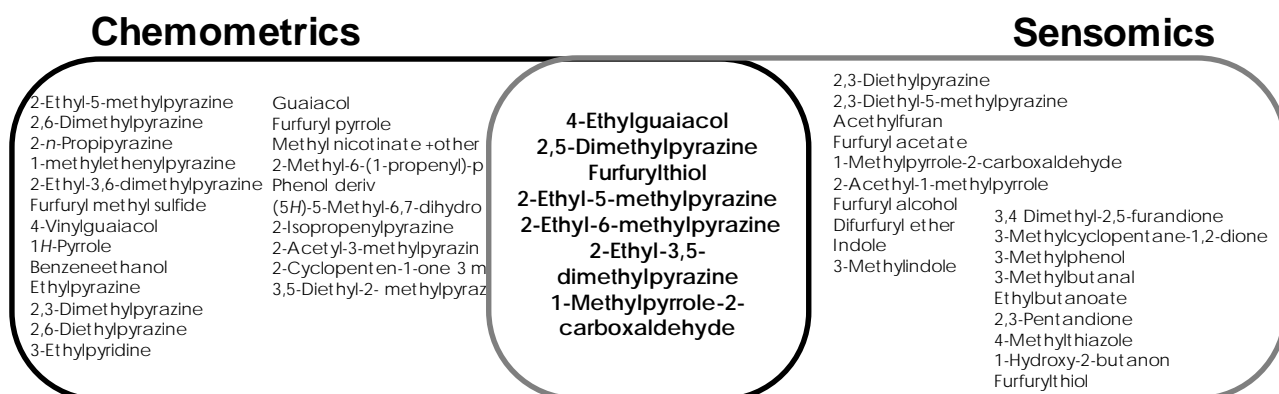
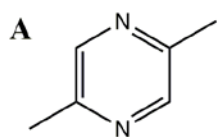
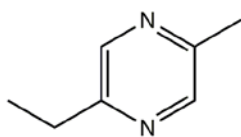


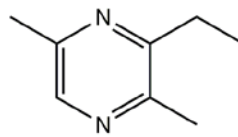
Figure 7



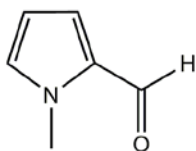
2,5-Dimethylpyrazine, **21**



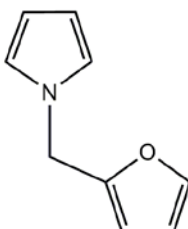
2-Ethyl-5-methylpyrazine, **27**



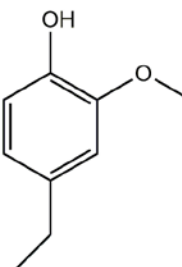
2-Ethyl-3,6-dimethylpyrazine, **33**



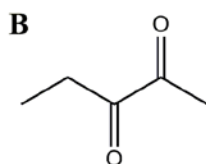
1-Methylpyrrole-2-carboxaldehyde, **55**



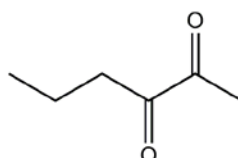
Furfurylpyrrole, **81**



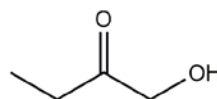
4-Ethylguaiacol, **92**



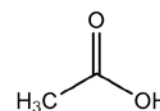
2,3-Pentanedione, **10**



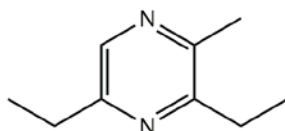
2,3-Hexandione, **13**



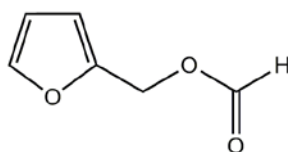
1-Hydroxy-2-butanone, **25**



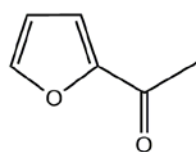
Acetic acid, **34**



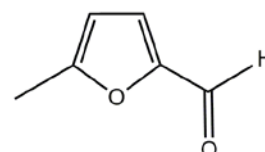
3,5-Diethyl-2-methylpyrazine, **39**



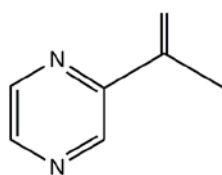
Furfuryl formate, **41**



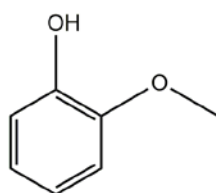
Acetylfuran, **42**



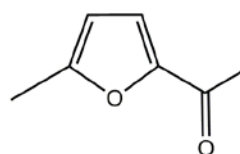
5-Methyl furfural, **49**



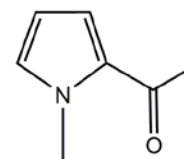
1-Methylethenylpyrazine, **51**



Guaiacol, **82**



2-Acetyl-5-methylfuran, **83**



1H-Pyrrole-2-carboxaldehyde, **91**

Table of Contents Graphic

