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Title: Comparison of the performances of handheld and benchtop near infrared spectrometers: application on the quantification of chemical components in maritime pine (*Pinus Pinaster*) resin

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1 **1 Introduction**

2 Maritime pine (*Pinus pinaster*) tapping (resin collection) was a prominent activity in France
3 from the 19th century until the 1970's [1]. Maritime pine covers in the Southwest of France
4 more than one million hectares [2]. After the 1970s, tapping drastically declines because its
5 lost its profitability, mainly because to the growth of the Chinese market [3,4]. Recently,
6 tapping reemerged [5] with new, mechanized tapping techniques, in a context with concerns
7 about harvesting in sustainable and environmentally friendly conditions [6].

8 Closed cup tapping is one of these techniques. The first works are related to (C. Courau,
9 1996) [7]. Closed cup tapping became increasingly popular in France and is currently being
10 improved [8]. Briefly described, a superficial incision using a circular saw removes a section
11 of the bark and of the secondary phloem, where the resin is formed [9]. Then, a stimulant
12 paste composed of natural acids is applied to activate resin exudation. Finally, a bottleneck
13 guides the drained resin into an airtight sealed plastic bag, which protects the resin from
14 impurities such as insects, sand, plant debris or rainwater, and limits evaporation.

15 Resin exudates abundantly [10] as a complex mixture of a volatile fraction (turpentine) and a
16 nonvolatile fraction (rosin) [11,12]. Turpentine consists of a few unsaturated hydrocarbon
17 monoterpenes, with smaller amounts of other monoterpenes [13,14]. Rosin is mainly
18 composed of diterpenic monocarboxylic acids, plus neutral components [15–17]. The various
19 components can be analyzed quantitatively using gas chromatography [18–21] and or liquid
20 chromatography [22,23]. These methods are used for quality control and to select higher
21 quality resin, but they are time-consuming and hard to use on-site. Considering this, the
22 present study looks for alternative analytical methods, including Near infrared (NIR)
23 spectroscopy in combination with chemometrics [24,25].

24 NIR spectroscopy is a non-destructive, reliable, and rapid tool for quantification, and can be
25 applied on portable devices [26]. Indeed, low cost handheld near-infrared spectrometer, such

26 as *SCiO* (*Consumer Physics*, Israel), has been reported in the literature as a reliable and
27 inexpensive technology, which facilitates its use on an industrial scale [27–32]. The objective
28 of this study is to assess the potential of *SCiO* as a direct and rapid analysis tool for the
29 quantification of the main chemical components of *Pinus pinaster* resin with chemometric
30 processing.

31 Partial Least Squares (PLS) regression was used to develop quantitative predictive models.
32 Those models were optimized various different spectral preprocessing methods. Then, the
33 performance of *SCiO* was compared to the baseline of a benchtop spectrometer.

34 **2 Materials and methods**

35 *2.1 Sample collection and conservation*

36 One hundred and twenty-five samples of maritime pine (*Pinus pinaster*) resin were harvested
37 in Biscarrosse (Landes, France) during the summer of 2018. They were collected by tapping
38 one hundred and twenty-five fifty years old trees using a closed cup tapping technique
39 patented by (L. Leneveu, 2002) [8]. Briefly described, the method consisted in having the
40 resin flow into a sealed plastic bag made of an ethylene vinyl alcohol (EVOH) inner film (70
41 μm thick) and a low-density polyethylene (LDPE) outer film (45 μm thick).

42 Once, the samples were stored in a box kept away from light and heat in order avoid chemical
43 alteration.

44 *2.2 Reference methods*

45 *2.2.1 Proportion of turpentine fraction in Pinus pinaster resin (% turpentine)* 46 *using a ventilated oven*

47 *For convenience, the relative proportion of turpentine and rosin fractions is designated here*
48 *collectively as the “Proportion of turpentine fraction”.*

49 The proportion of turpentine fraction in maritime pine (*Pinus pinaster*) resin (*% turpentine*)
50 was quantified using a ventilated oven.

51 The *% turpentine* was an important data for this study, because, the chemical composition
52 was determined with two different analytical instruments, and the chemical composition
53 pertains respectively to each fraction. Therefore, *% turpentine* is an indicator of the actual
54 amount of the chemical components in each of the fractions.

55 Briefly, 2 g of resin were poured in a aluminium cup. The weight difference before and after
56 drying was used to determine *% turpentine*. Each sample was placed in a ventilated oven at a
57 temperature close to the boiling point of monoterpenes, for a duration sufficient to provoke its
58 evaporation. Specifically, the samples were placed at 150 °C for 30 min in the ventilated
59 oven.

60 *2.2.2 Chemical composition of the turpentine as determined via Gas* 61 *Chromatography coupled to a Flame Ionization Detector (GC–FID)* 62 *analysis and sample preparation*

63 The chemical composition of the turpentine fraction from maritime pine (*Pinus pinaster*) resin
64 was quantified using a Perkim-Elmer Clarus 500 gas chromatograph (GC) coupled to a Flame
65 Ionization Detector (FID), and a Perkim-Elmer Elite-5MS capillary column (30 m x 0,25 mm
66 x 0,5 µm film thickness).

67 To prepare the samples, the plastic bag containing the resin was homogenized manually for
68 several minutes until the turpentine and rosin were completely mixed. Then, 10 mL of the
69 resin were poured in a cylindrical glass vial (h = 50 mm, outer diameter = 22 mm). After three
70 days, 0.5 mL of supernatant containing turpentine was diluted with 1.5 ml of hexane, which
71 was, in turn, stirred in an ultrasonic bath for 1 min, then filtered through a 0.2 µm nylon filter
72 before injecting. 1 µL of this solution.

73 The experimental conditions developed in the laboratory were as follow: both injector and
74 detector temperatures were set at 290 °C; oven temperature program, 50 to 150 °C (2 °C/min),
75 then 150 to 320 °C (10 °C/min); hydrogen was used as carrier gas. The first ramp was used to
76 elute the volatile components of the turpentine, the second ramp was used to clean the
77 column.

78 Between each sample injection, two flash cleaning programs with acetone and hexane were
79 applied to remove any residue (50 to 250 °C (15 °C/min)).

80 For the identification of the components of the turpentine fraction, Kovats's linear retention
81 index was calculated from the injection of a homologous series of hydrocarbons (C8 – C20)
82 and compared with literature data [33], in accordance with ASTM D6730 [34]. For the
83 quantitative analysis, the respective rates were expressed as percentages.

84 *2.2.3 Chemical composition of the rosin fraction determined via High-*
85 *Performance Liquid Chromatography coupled to Diode Array*
86 *Detectors (HPLC-DAD) and sample preparation*

87 The chemical composition of the rosin fraction from maritime pine (*Pinus pinaster*) resin was
88 quantified using High-Performance Liquid Chromatography coupled to a Diode Array
89 Detector (HPLC-DAD). A methodology similar to the ones already reported was used
90 [35,36]. Briefly, the plastic bag containing the resin was homogenized manually for several
91 minutes until the turpentine and rosin were completely mixed. Then, 1 % w/v of the sample
92 was diluted in Methanol. 10 µL of this solution was injected in a Thermo Scientific Ultimate
93 3000 chromatographic unit equipped with a Thermo Scientific LC Acclaim PolarAdvantage II
94 C18 column (5 µm, 150 x 4.6 mm), and a Diode Array Detector. The separation was carried
95 out at 20 °C with a binary gradient mixture of solvent A (methanol + 1.0 % formic acid) and
96 solvent B (water + 1.0 % formic acid). A flow rate of 300 µl/min was used with a gradient

97 program as follow: 0-2 min (60 % of A); 2-17 min. (60-80 % of A); 17-34 min. (80 % of A);
98 34-48 min. (80-100 % of A); 48-67 min. (100 % of A); equilibrated (60 % of A).
99 The methodologies described by (Lee et al., 1997; Kersten et al., 2006) [22,23] were used for
100 identification and quantification of the chemical components of the rosin fraction.

101 2.3 Near infrared (NIR) acquisition

102 Near infrared (NIR) acquisition was performed using a benchtop spectrometer and a handheld
103 spectrometer, respectively, *MultiPurpose Analyzer I* (Bruker, USA) and *SCiO* (*Consumer*
104 *Physics*, Israel).

105 *MultiPurpose Analyzer I* is a Fourier transform near infrared (FT-NIR) spectrometer
106 implemented with an integrating sphere. The spectral range of acquisition was between
107 12,500 to 4,166 cm^{-1} (780 to 2400 nm) with a nominal resolution of 8 cm^{-1} . For the spectral
108 acquisition, resin was poured in a cylindrical glass vial (h = 50 mm, outer diameter = 22 mm),
109 and placed over the sphere window, with an average of 16 scans for each spectrum.

110 *The SCiO* handheld spectrometer [37] operated in a spectral range between 13,514 to 9,346
111 cm^{-1} (740 to 1070 nm) with values every 1 nm and an optical resolution of 30 nm [38]. The
112 resin samples were scanned directly through the sealed plastic bag using an accessory
113 provided by *Consumer Physics* to avoid ambient light interference, and also to ensure a
114 constant distance of 10 mm between the light source and the sample. For each sealed plastic
115 bag, the spectrum was calculated as the median of six measurements.

116 As the *SCiO* is a cloud-based device, *Consumer Physics* proposes a commercial online
117 toolkit, which is required for spectra acquisition and download them. This online toolkit is
118 also useful to create online mathematical models, which can be implemented in a mobile
119 application using the *Software Development Kit* provided by *Consumer Physics*. Yet, this
120 application was not used in the present study.

121 2.4 *Multivariate Data Analysis*

122 Fig. 1 details the process used during the Multivariate Data Analysis. The same methodology
123 was applied on both spectrometers, in order to compare their quantitative predictive ability.

124 2.4.1 *Preprocessing*

125 During spectral data acquisition, scattering of photons leads to many physical phenomena
126 (lengthening of the optical path, noise) that need to be corrected with spectra preprocessing
127 algorithms [39] to limit the influence of physical phenomena on the relevant properties [40].
128 Such effects include baseline drift, nonlinearity, curvilinearity, additive and multiplicative
129 effects, and irrelevant variations in the spectra [40]. Thus, several preprocessing techniques
130 were applied in order to increase the accuracy of the predictive models: Standard Normal
131 Variate (SNV), Detrend (DT2), combination of SNV and DT2 [41], Multiplicative Scatter
132 Correction (MSC) [42], and Savitzky-Golay's first and second derivatives [43].

133 2.4.2 *Subset Selection*

134 Subset selection algorithms were used to extract calibration and independent validation
135 subsets from a dataset [44]. The DUPLEX algorithm [45] promotes sample
136 representativeness, ensuring that the selected spectra are uniformly distributed in the
137 multidimensional data space and that the dependent variable has the same statistics
138 characteristics (mean, variance, range, etc.).

139 In the first step, the two spectra most distant from each other are selected and placed in the
140 calibration subset. On the remaining spectra, the following pair of spectra most distant from
141 each other are selected for the validation subset. By alternating subsets, the procedure
142 continues to select a single spectrum for each subset of data. The selected spectrum is the one
143 farthest from the spectra already selected within the subset. Once the required number of

144 samples is reached in the validation subsets, the remaining samples are placed in the
145 calibration subset.

146 With this procedure, the dataset was split as follow: 70 % in the calibration subset, and 30%
147 in the validation subset.

148 *2.4.3 Modelling Phase*

149 Partial Least Squares (PLS) regression with Nonlinear Iterative Partial Least Squares
150 (NIPALS) algorithm is the favorite for regression in NIR applications, because of its ability to
151 analyze high-dimensional and multi-collinear data [46,47]. Its purpose is to use independent
152 variables (X) to predict a dependent variable (y): the spectra (X) are used to predict the
153 analytical reference values (y). To achieve this goal, it will attempt to meet three objectives:
154 (i) explain X ; (ii) explain y ; (iii) find relationships between X and y . Nonlinear Iterative
155 Partial Least Squares (NIPALS) has been used as algorithm to perform PLS.

156 In order to evaluate the quantitative predictive ability of Partial Least Squares (PLS) models,
157 several merit scores were computed. The coefficient of determination gave a measure of
158 linearity of the prediction based either on the calibration subset (R_{cal}^2 ; R_{CV}^2), or on the
159 validation subset (R_{Val}^2). Root Mean Square Error of Calibration, Cross-Validation and
160 Prediction (respectively, RMSEC, RMSECV and RMSEP) were used to measure the accuracy
161 of the prediction calculated on both the calibration and validation subsets.

162 Another figure of merit, the Ratio of standard error of Performance to standard Deviation
163 (RPD), was computed to classify the applicability of the models. According to (Williams,
164 2014) [48], higher RPD values were associated with better quantitative prediction.

165 General rules emerge to classify the applicability of the models: with $2.5 \leq RPD < 3.0$, the
166 quantitative model makes approximate quantitative predictions (screening); with $3.0 \leq RPD <$
167 3.5 , good quantitative predictions (quality control); for $3.5 \leq RPD < 4.1$, very good

168 quantitative predictions (process control); and $RPD \geq 4.1$ indicates an excellent quantitative
169 predictive model.

170 2.4.4 Software

171 Chemometric models construction was carried out using Matlab 2019a (Mathworks Inc.,
172 USA) with the SAISIR toolbox [49], and all the scripts were designed in-house.

173 3 Results and discussion

174 3.1 Chemical composition and % turpentine of maritime pine (*Pinus pinaster*) resin

175 Table 1 list the values of the studied parameters of maritime pine (*Pinus pinaster*) samples:
176 main chemical components of the turpentine and rosin fractions, and proportion of the
177 turpentine fraction.

178 Concerning the turpentine fraction, the results obtained via GC-FID showed that the analyzed
179 turpentine of *Pinus pinaster* is mainly composed of unsaturated hydrocarbon monoterpenes,
180 above all α -pinene and β -pinene: the α -pinene content was $66.2 \pm 9.0 \%$ and the β -pinene
181 content was $18.5 \pm 8.5 \%$. (Ghanmi et al., 2005) [13], comparing the turpentine content of
182 maritime pine (*Pinus pinaster*) and of Aleppo pine (*Pinus halepensis*) from Morocco, report
183 similar composition values for α -pinene and β -pinene as main components of turpentine: 78.7
184 % for α -pinene, and 7.3 % for β -pinene.

185 Concerning the rosin fraction, the results from HPLC-DAD show that the analyzed rosin of
186 *Pinus pinaster* is mainly composed of diterpenic monocarboxylic acids, such as levopimaric
187 acid, with a content of $62.1 \pm 5.9 \%$. (Arrabal et al., 2005) [50] monitored the oleoresin
188 chemical composition of 150 Spanish *Pinus pinaster* trees aged of 33 years old, from thirty
189 sites. Authors reported similar composition values with levopimaric acid as the main
190 constituent ranging from 41.7 to 45.3 %.

191 The turpentine content (*% turpentine*) was $34.3 \pm 6.6 \%$, also in agreement with the literature:
192 (Arrabal et al., 2005) [50] found *% turpentine* values ranging from 27.7 to 30.3 %.

193 3.2 NIR spectra

194 As reminded by (Y. Ozaki, 2012) [51], near infrared can be divided in three regions: region I
195 ($800 - 1200 \text{ nm}$; $12500 - 8500 \text{ cm}^{-1}$), region II ($1200 - 1800 \text{ nm}$; $8500 - 5500 \text{ cm}^{-1}$) and
196 region III ($1800 - 2500 \text{ nm}$; $5500 - 4000 \text{ cm}^{-1}$). Those regions have specific spectral
197 features, covering mainly electronic transitions, overtones and combination bands [52].

198 The benchtop *MPA I* spectrometer covers the $12,500 - 4,166 \text{ cm}^{-1}$ range (780 to 2400 nm),
199 which roughly corresponds to all these three regions. Along the spectra acquired with the
200 *MPA I*, the *CH* first overtone, third overtone, deformation band and combination band; *OH*
201 second overtone and *C = O* first and fourth overtone are observed.

202 The handheld *SCiO* spectrometer covers a narrow range from $13,514$ to 9346 cm^{-1} (740 to
203 1070 nm), which covers the first region (Region I), also called “*near infrared*”, where *CH*
204 third overtone and *OH* second overtone are observed. In fact, the *SCiO*'s capacity in the
205 visible domain and the NIR domain are limited [32]. From this information, it is assumed that
206 *MPA I* and *SCiO* spectrometers can consistently detect the same vibrational bands at different
207 overtones.

208 Table 2 reports the vibrational bands of *Pinus pinaster* resin. The table was drafted based on
209 the chemical structure of its major components, the spectra shapes, and the literature [53,54].

210 3.3 Modelling Phase

211 Statistics of Partial Least Squares (PLS) regression are presented in Table 3.

212 PLS regression was applied on calibration subsets to develop quantitative predictive models.

213 In PLS modeling, Latent Variables (LVs) were calculated and considered as new eigenvectors

214 to reduce the dimensionality and compress the original spectral data. The number of LVs was
215 determined as the one that provided the lowest RMSECV using a leave-one-out cross-
216 validation. Once developed, the model was applied to validation subsets, which had not been
217 used during the calibration procedures. Then, the predictive ability of each model was
218 assessed by external validation on the validation subsets.

219 As a rule, a good model should have higher R_{Cal}^2 , R_{CV}^2 , R_{Val}^2 and RPD values, and lower
220 RMSEC, RMSECV and RMSEP. Here, the quantitative predictive ability of the model was
221 selected based on highest RPD values.

222 3.3.1 Benchtop spectrometer: MultiPurpose Analyzer I (Bruker, USA)

223 Figure 2 (a) shows the raw spectra acquired with the *MultiPurpose Analyzer I*. Figure 2 (b to
224 g) shows the preprocessed spectra. The raw and preprocessed spectra highlight many
225 vibrational bands, which contain all the information needed for the modelling phase.

226 As seen in Table 3, all the parameters values of the coefficients of determination calculated
227 between reference and predicted data on either calibration or validation subsets are excellent
228 ($R_{Cal}^2 > 0.8$; $R_{CV}^2 > 0.8$; $R_{Val}^2 > 0.8$). In this case, PLS regression models predictions are well
229 correlated to the references ones. RMSEC, RMSECV and RMSEP values are low in
230 accordance with the reference data. In addition, they are close, which shows that the PLS
231 regression models are robust. RPD statistics give poorest performance with PLS regression
232 models computed without preprocessing (raw data). This means that spectral preprocessing is
233 mandatory to improve the predictive ability of all models. Concerning the RPD values, all
234 parameters are classified in two groups. In the first group, $RPD \geq 4.1$, indicating excellent
235 quantitative predictive models for α -pinene, β -pinene, and abietic and neoabietic acids. In the
236 second group, the RPD ranges from 3.5 to 4.1, indicating very good quantitative predictions,
237 for levopimaric acid and % turpentine.

238 Concerning the preprocessing, Detrend (DT2) gives better predictive ability for a mixture of
239 abietic and neoabietic acids (RPD = 4.0); Savitzky–Golay first derivatives (SG1) give better
240 predictive ability for α -pinene (RPD = 4.7) and levopimaric acid (RPD = 4.0); Savitzky–
241 Golay second derivatives (SG2) give better predictive ability for β -pinene (RPD = 5.0) and %
242 *turpentine* (RPD = 3.5).

243 3.3.2 Handheld spectrometer: *SCiO* (Consumer Physics, Israel)

244 Figure 3 (a) shows the raw spectra acquired with the *SCiO*. The raw spectra seem flat and did
245 not exhibit any characteristic vibrational bands except for *OH* at 957 nm (10,449 cm^{-1}). This
246 is seemingly due to physical phenomena, such as scattering effects and overlapping signals
247 [55,56].

248 In practice, *SCiO* lacks repeatability and reproducibility. For example, the same sample area
249 can be scanned (without touching or moving the device) several times, causing intensity shift.
250 (Subedi *et al.*, 2020) [38] is cited as a first attempt to test the repeatability of *SCiO*, and two
251 other spectrometers: *MicroNIR* (Viavi, USA) and *F750* (Felix Instruments, USA). There the
252 authors expressed the repeatability as the standard deviation of absorbance of the highest
253 signal across the wavelength range monitored. Standard deviation was computed on 20
254 repeated measures of a PTFE reference material. Standard deviation was 0.04, 0.22 and
255 0.40 m Absorbance units for the *F750*, *MicroNIR* and *SCiO* spectrometers respectively. The
256 values obtained with the *SCiO* were much higher than with the others two spectrometers. It is
257 thus necessary, for each sample, to acquire several spectra, and to use a statistical method
258 (*mean*, *median*) in order to have a representative spectrum, and also, to apply preprocessing
259 algorithms. Once the spectra are preprocessed, vibrational bands are highlighted (Figure 3: b -
260 g).

261 Similarly, with the PLS regression models developed for the benchtop spectrometer for all
262 parameters, the values of coefficients of determination (R_{Cal}^2 ; R_{CV}^2 ; R_{Val}^2) show good

263 agreement between prediction and reference values. RMSEC, RMSECV and RMSEP values
264 were higher than those obtained with the benchtop device, and show some discrepancy,
265 suggesting that PLS regression models cannot be as robust as with the benchtop device.
266 Looking at RPD statistics, spectral preprocessing is also required to improve the predictive
267 ability of all models. As shown in Table 3, the five parameters can be classified into two
268 groups. In the first group, the RPD ranges from 3.0 to 3.5, which indicate some good
269 quantitative predictive ability for quality control. This group includes all major components of
270 the resin, such as α -pinene, and levopimaric, abietic and neoabietic acids. In the second group,
271 the RPD ranged between 2.5 and 3.0, i.e. β -pinene and % *turpentine* were less correctly
272 predicted.

273 Concerning the preprocessing, Detrend (DT2) gives better predictive ability for the mixture of
274 abietic and neoabietic acids (RPD = 3.01). Combination of Standard Normal Variate and
275 Detrend (SNV + DT2) give better predictive ability for % *turpentine* (RPD = 3.03).
276 Multiplicative Scatter Correction (MSC) gives better predictive ability for levopimaric acid
277 (RPD = 3.09). Savitzky–Golay second derivatives (SG2) give better predictive ability for α -
278 pinene (RPD = 3.16) and β -pinene (RPD = 2.82).

279 **4 Conclusion**

280 The *SCiO* handheld NIR spectrometer was studied as a potential tool to quantify the chemical
281 components of maritime pine (*Pinus pinaster*) resin, in view of its use as a quality control tool
282 for the tapping industry.

283 This study looked at the performance of the handheld *SCiO* spectrometer in comparison with
284 a benchtop *MPA I* spectrometer, and evaluated the performance based on statistical
285 parameters.

286 Although, *SCiO* and *MPA I* work in different NIR regions, PLS regression models can be
287 used to quantify major resin components, such as, α -pinene, β -pinene, levopimaric, abietic

288 and neoabietic acids, and % *turpentine*. Results shown that spectral preprocessing is
289 mandatory to increase the predictive ability of the PLS regression models.

290 Considering the selected PLS models: the coefficients of determination (R_{Cal}^2 ; R_{CV}^2 ; R_{Val}^2)
291 show good agreement between prediction and reference values for both, *SCiO* and *MPA I*
292 spectrometers with values higher than 0.8; RMSEC, RMSECV and RMSEP values were
293 higher for the *SCiO* compared to the *MPA I*, and they also show some discrepancy, suggesting
294 that PLS regression models for *SCiO* cannot be as robust as *MPA I* models; RPD statistics
295 values were lower for the *SCiO* compared to the *MPA I* – the RPD values for *MPA I* showed
296 an excellent quantitative predictive ability, whereas those for *SCiO* have a good quantitative
297 predictive ability for quality control purposes.

298 Considering the overall instrument parameters (wavelength, resolution, size, cost), the *SCiO*
299 spectrometer showed very good results. Additionally, the *SCiO* is a handheld spectrometer,
300 and can be easily used on-site. Thus, the *SCiO* could be a useful tool to predict main chemical
301 components of maritime pine (*Pinus pinaster*) for quality control in the tapping industry.

302

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310 **Declaration of competing interest**

311 The authors declare no actual or potential conflicts of interests.

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Figure 1 Detailed overview of the Multivariate Data Analysis.

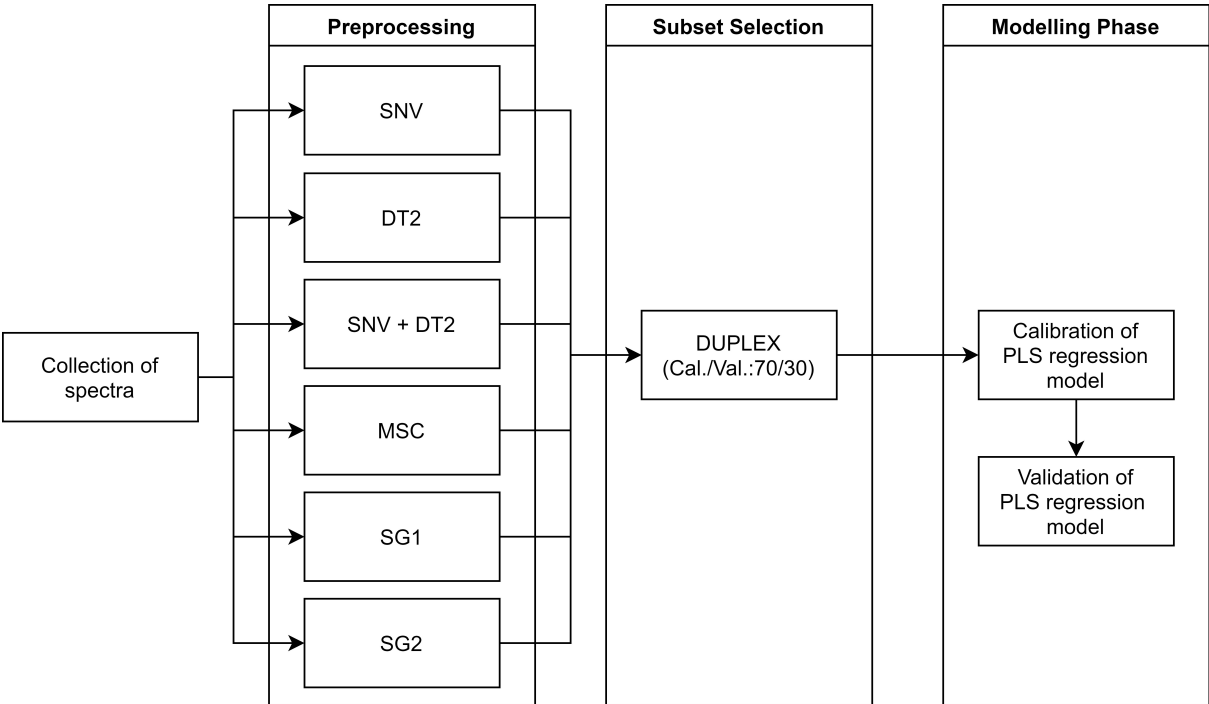


Figure 2 Different preprocessing algorithms were applied to the raw spectra acquired with *SCiO* (*Consumer Physics*, Israel). (a) Raw spectra; (b) SNV preprocessed spectra; (c) DT2 preprocessed spectra; (d) SNV + DT2 preprocessed spectra; (e) MSC preprocessed spectra; (f) SG1 preprocessed spectra; (g) SG2 preprocessed spectra.

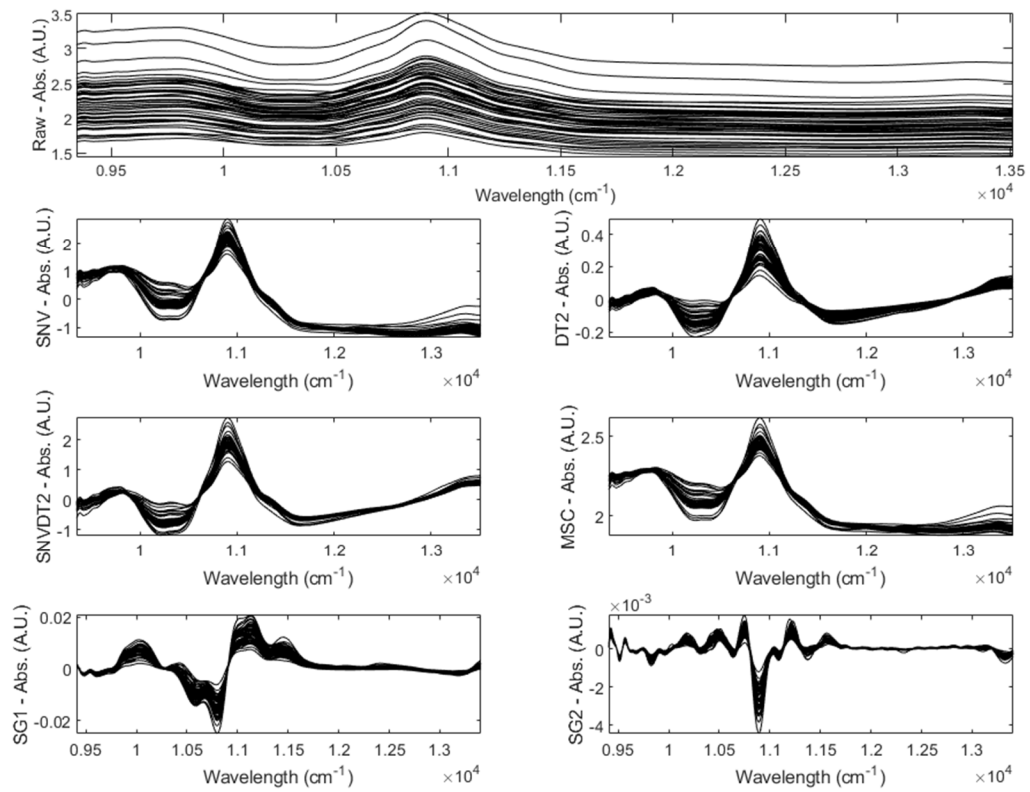


Figure 3 Different preprocessing algorithms were applied to the raw spectra acquired with *MultiPurpose Analyzer I* (Bruker, USA). (a) Raw spectra; (b) SNV preprocessed spectra; (c) DT2 preprocessed spectra; (d) SNV + DT2 preprocessed spectra; (e) MSC preprocessed spectra; (f) SG1 preprocessed spectra; (g) SG2 preprocessed spectra.

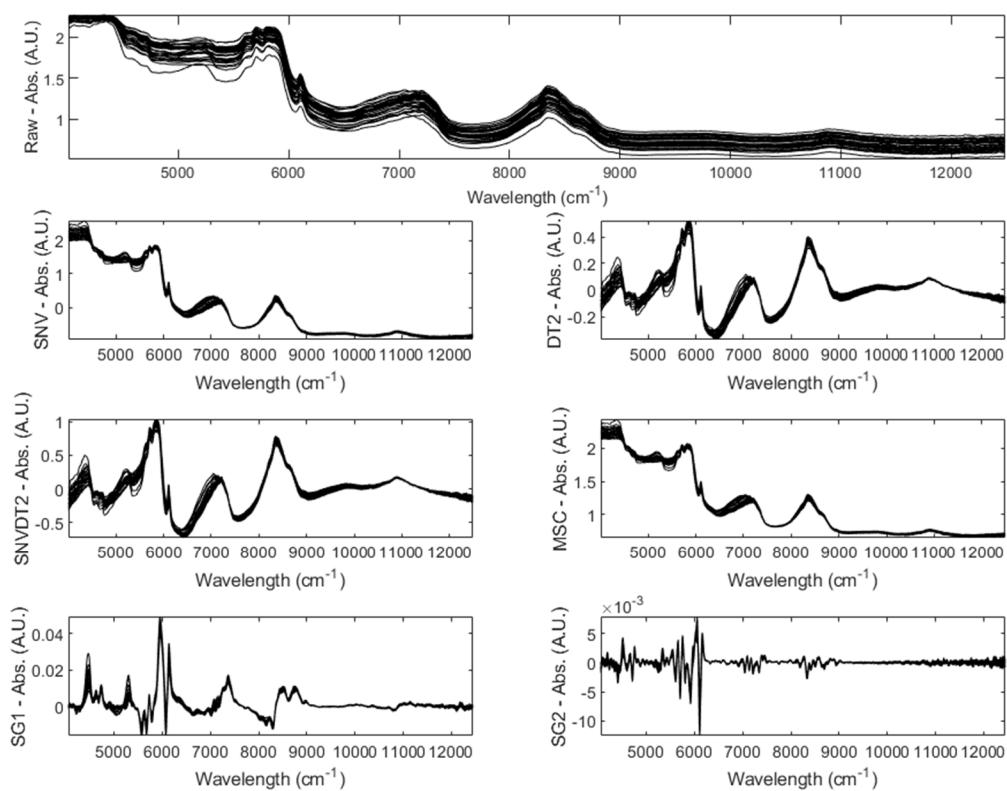


Table 1 Values of the parameters of the analyzed samples of maritime pine (*Pinus pinaster*): main chemical components of the turpentine and rosin fractions, and proportion of the turpentine fraction.

	Parameters	Number of samples	Minimum (%)	Maximum (%)	Mean (%)	Standard deviation (%)
Turpentine Chemical Composition	α -pinene	94	44.05	84.37	66.16	9.01
	β -pinene		3.24	37.47	18.47	8.45
	Myrcene or/and δ -3 carene		0.04	0.52	0.28	0.11
	Limonene		0.88	6.12	4.08	0.68
	γ -terpinene		0.64	2.19	1.42	0.30
Rosin Chemical Composition	Levopimaric acid	49	49.66	75.25	62.10	5.93
	Abietic and Neoabietic acids		24.75	50.34	37.90	5.93
% Turpentine	% Turpentine	112	15	52.8	34.25	6.58

Table 2 Band assignments for the chemical components of maritime pine (*Pinus Pinaster*) resin.

Device	Wavenumber		Functional group	Possible band assignments for:	
	(cm^{-1})	(nm)		Turpentine constituents	Rosin constituents
MultiPurpose Analyzer I	10891	918	CH methylene (CH_2)		
	9889	1011	OH from tertiary alcohols ($C - OH$)		
	8662	1154	C = O from Carbonyl ($C = O$)		
	7211	1387	CH methyl associated with aromatic ($Ar - CH_3$)		
	6911	1447	CH aromatic (Ar)		
	6101	1639	CH from vinyl group as ($CH_2 = CH -$)		
	5816	1719	CH methyl (CH_3)		
	5708	1752	CH methylene (CH_2)		
	5600	1786	CH methylene (CH_2)		
	5222	1915	C = O (carbonyl) from acid ($C = OOH$)		
	4535	2205	CH aromatic (Aryl)		
	4420	2262	CH (CH Bending)		
	SCrO	11074	903	CH methylene (CH_2)	
10787		927	CH methylene (CH_2)		
10449		957	OH Alkyl Alcohols ($R - C - OH$)		
9843		1016	OH from tertiary alcohols as ($-C - OH$)		
9443		1059	OH with hydrogen bonding ($R - C - OH$)		

Table 3 Statistics of Partial Least Squares (PLS) regression models.

	Preprocessing	SCiO (Consumer Physics, Israel)								MultiPurpose Analyzer I (Bruker, USA)							
		LVs	R^2_{Cal}	R^2_{CV}	R^2_{Val}	RMSEC	RMSECV	RMSEP	RPD	LVs	R^2_{Cal}	R^2_{CV}	R^2_{Val}	RMSEC	RMSECV	RMSEP	RPD
α -pinene	RAW	9	0,87	0,83	0,46	3,33	3,71	5,57	1,23	5	0,86	0,87	0,81	3,28	3,25	3,81	2,33
	SNV	10	0,90	0,86	0,64	2,71	3,33	6,57	1,53	4	0,90	0,89	0,89	2,88	2,92	3,10	2,87
	DT2	10	0,93	0,92	0,85	2,36	2,57	4,13	2,28	6	0,94	0,92	0,94	1,99	2,54	2,85	3,63
	SNV + DT2	12	0,91	0,92	0,89	2,40	2,57	3,49	3,09	6	0,94	0,94	0,92	2,10	2,13	2,79	3,42
	MSC	9	0,86	0,86	0,81	3,31	3,38	3,96	2,35	4	0,91	0,90	0,91	2,79	2,87	3,03	2,82
	SG1	8	0,95	0,92	0,76	1,95	2,47	4,56	1,93	6	0,97	0,97	0,95	1,53	1,66	2,00	4,70
	SG2	5	0,93	0,92	0,91	2,26	2,47	3,24	3,16	4	0,96	0,95	0,94	1,72	1,91	2,44	4,16
β -pinene	RAW	10	0,92	0,87	0,47	2,35	3,07	5,49	1,35	10	0,96	0,96	0,94	1,61	1,78	2,19	3,69
	SNV	10	0,90	0,88	0,52	2,70	2,95	7,63	1,11	9	0,97	0,96	0,94	1,47	1,59	2,01	4,12
	DT2	8	0,89	0,90	0,85	2,71	2,70	3,64	2,52	5	0,88	0,88	0,91	2,71	2,90	3,13	3,11
	SNV + DT2	9	0,90	0,89	0,86	2,39	2,75	3,99	2,54	7	0,96	0,94	0,93	1,69	2,08	2,38	3,83
	MSC	9	0,89	0,87	0,84	2,58	2,99	3,88	2,42	8	0,96	0,95	0,95	1,62	1,91	1,97	4,45
	SG1	10	0,96	0,95	0,85	1,62	1,91	3,29	2,66	8	0,99	0,98	0,89	0,78	1,13	2,99	3,09
	SG2	4	0,93	0,92	0,87	2,16	2,45	3,26	2,82	4	0,96	0,96	0,96	1,66	1,79	1,91	4,96
Levopimaric acid	RAW	6	0,84	0,86	0,81	3,77	4,27	3,45	1,98	9	0,92	0,92	0,92	2,48	2,67	2,60	3,42
	SNV	6	0,80	0,84	0,85	3,86	4,22	3,99	2,51	7	0,93	0,93	0,94	2,38	2,76	2,29	3,87
	DT2	5	0,82	0,84	0,87	3,71	4,25	3,70	2,55	9	0,95	0,94	0,94	1,95	2,15	2,72	3,81
	SNV + DT2	4	0,76	0,78	0,88	4,01	4,09	3,77	2,85	5	0,89	0,90	0,83	2,90	2,88	4,26	2,24
	MSC	6	0,78	0,81	0,89	4,09	4,66	3,01	3,09	6	0,90	0,90	0,95	2,89	2,80	2,27	3,75
	SG1	6	0,89	0,93	0,79	2,89	3,04	4,14	2,13	6	0,93	0,93	0,94	2,43	2,65	2,38	3,95
	SG2	5	0,85	0,86	0,86	3,26	3,69	3,93	2,60	4	0,90	0,91	0,94	2,69	2,91	2,72	3,72
Abietic and neoabietic acids	RAW	7	0,86	0,91	0,86	3,50	3,61	3,00	2,28	8	0,93	0,93	0,94	2,29	2,59	2,34	3,80
	SNV	6	0,72	0,73	0,59	4,76	5,39	6,63	1,51	9	0,94	0,94	0,96	2,17	2,53	2,06	4,30
	DT2	8	0,86	0,88	0,90	3,23	3,53	3,13	3,01	7	0,95	0,95	0,95	1,87	1,98	2,59	3,99
	SNV + DT2	3	0,28	0,29	0,65	7,08	7,44	7,34	1,47	7	0,95	0,96	0,94	2,06	2,18	2,24	4,25
	MSC	7	0,61	0,61	0,82	6,56	6,89	3,98	2,34	8	0,94	0,95	0,95	2,26	2,57	2,17	3,92
	SG1	6	0,91	0,91	0,84	2,67	2,62	3,52	2,51	4	0,90	0,91	0,90	2,88	3,04	2,94	3,19
	SG2	3	0,85	0,86	0,88	3,22	3,78	3,56	2,87	3	0,90	0,90	0,94	2,66	2,96	2,64	3,83
% Turpentine	RAW	7	0,89	0,91	0,79	3,09	3,25	3,35	2,04	5	0,91	0,92	0,90	2,63	2,58	2,82	3,16
	SNV	6	0,85	0,85	0,68	3,37	3,92	6,87	1,46	6	0,89	0,90	0,87	2,98	3,11	3,24	2,74
	DT2	8	0,88	0,90	0,90	3,07	3,34	3,17	2,98	7	0,92	0,92	0,90	2,42	2,72	3,42	3,02
	SNV + DT2	5	0,78	0,82	0,89	3,86	4,06	3,56	3,03	6	0,90	0,91	0,88	2,78	3,04	3,30	2,89
	MSC	7	0,73	0,79	0,78	4,98	5,25	4,67	1,99	6	0,89	0,91	0,92	3,09	3,42	2,96	2,88
	SG1	4	0,90	0,92	0,83	2,87	3,29	3,56	2,48	5	0,89	0,91	0,91	3,03	3,20	2,73	3,44
	SG2	5	0,87	0,88	0,89	3,05	3,28	3,42	2,99	4	0,89	0,91	0,92	2,86	3,07	2,94	3,45

Graphical Abstract

