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1 The Potential of Handheld Near Infrared 2 Spectroscopy to detect food adulteration: 3 Results of a global, multi-instrument inter- 4 laboratory study

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18

19 Abstract

20 Fraud in the food supply system will be exacerbated by shortages caused by climate change and
21 COVID-19's impact. The dried herbs market exemplifies complex supply chains attractive to
22 criminals seeking financial gain. Real-time remote testing is achievable through development of
23 globally accessible chemometric models for portable near infrared devices, deployed throughout
24 supply chains. This study describes building of models for detection of oregano adulteration, on
25 portable near infrared devices, and comparison to a laboratory-based Fourier-Transform Infrared
26 spectroscopy method. 33/34 portable devices were able to correctly classify 5 out of 6 samples
27 successfully with all adulterated samples being correctly classified following the use of appropriate
28 transferability pre-processing routines. The devices native setup shows limited ability to perform a true
29 screening of oregano using the setup offered. However modifications to the setup could in the future offer
30 a solution that facilitates fit-for-purpose real time detection of adulterated samples within the
31 supply chain.

32 Keywords

33 Portable Near Infrared Spectroscopy; Chemometric models; Discriminant analysis; Food
34 adulteration testing; Global Inter-laboratory study; Herbs and spices; Oregano adulteration

35 1 Introduction

36 Food Fraud is a global problem with incidents manifesting differently. These include: addition of
37 chemical additives to simulate a given parameter or confer a preferred attribute; substitution;
38 concealment of inferior quality attributes; re-labelling to infer premium quality eg free-
39 range/organic; or the manipulation of dates (Wisniewski & Buschulte, 2019). Despite its ubiquitous
40 nature the lack of a universal definition poses a challenge for economic analysis (Ehmke, Bonanno,
41 Boys, & Smith, 2019) and indeed consistent reporting of food fraud events. It has previously been
42 reported that the estimated global cost to the food industry lies somewhere between \$10 and \$40

43 billion however these estimates usually refer only to the market value of seizures and does not
44 take into account the impact of fraudulent activities on the relevant economies (Rocchi, Romano,
45 Sadiddin, & Stefani, 2020). In reality these figures represent a fraction of the true cost, because it
46 is impossible to know the full scale of food fraud and to assess the long-term effects of
47 reputational damage. Food fraud will occur when there is an opportunity, a means to perpetrate
48 and a motivation and an economic gain. It is often observed in commodities that have high
49 commercial value or are in high demand but, for some reason, have a scarcity of availability.

50 Dried herbs have multiple business-to-business and business-to-customer applications in food
51 processing, cosmetics and medicine. The global dried herbs market is expected to reach US\$ 4.1
52 billion by 2026 (TransparencyMarketResearch, 2018). This growth is driven by, amongst other
53 things, an increased appetite for processed foods and convenience foods brought about through
54 growing consumer disposable income (TransparencyMarketResearch, 2018). Economically
55 Motivated Adulteration (EMA) occurs especially in complex supply chains for foodstuffs that are in
56 high demand and showing increasing price trends (Galvin-King, Haughey, & Elliott, 2018). Oregano,
57 mostly associated with Mediterranean cuisine, is one such herb.

58 Several publications are available describing the non-targeted analysis of fraud in Oregano
59 including one by Black, Haughey, Chevallier, Galvin-King, & Elliott, (2016) and another by
60 Rodionova & Pomerantsev, (2020). Black et al., (2016) reported a Fourier-Transform Infrared
61 spectroscopy (FT-IR) method for the detection of EMA in oregano with a Limit of Detection of 13%.
62 That study described a retail survey that revealed over 24% of tested samples were adulterated
63 (Black et al., 2016). Following the study the FT-IR method gained ISO 17025 accreditation and is
64 being used to test a range of complex supply chains for fraud
65 (UnitedKingdomAccreditationService, 2019). Based on this research the authors were approached
66 by stakeholders in the food sector about in-field applications. Thus, a research project was

67 undertaken into the application of portable or hand-held Near Infrared spectroscopy (NIR) as a
68 means of conducting food authenticity analysis in a fast, reliable, and real time mode.

69 NIR has been widely used to address process control and quality control in the food industry
70 (McGrath et al., 2018). Historically this had been performed using benchtop or inline instruments.
71 Recently devices have been produced with smaller footprints to meet the increased demand for
72 portability. However, these devices typically do not match the performance of the benchtop
73 devices due to the restricted technical specifications that permit miniaturisation. Vendors of
74 integrated portable devices include, amongst others, Consumer Physics (ConsumerPhysics, 2020),
75 Neospectra (NeoSpectra, 2020), Tellspec (Tellspec, 2020), Thermo Fisher Scientific
76 (ThermoFisherScientific, 2020), and Viavi Solutions (ViaviSolutions, 2020). The spectra from these
77 devices can be used with either their own software or, in many instances, external software to
78 develop chemometric models for classification of adulteration or abnormality, in the case of non-
79 targeted analysis.

80 Ideally models developed can be applied to multiple instruments, preferably on devices from
81 different manufacturers but essentially on multiple devices from the same manufacturer avoiding
82 the need for individual instrument calibrations. In this way, one model can be created and
83 deployed across multiple instruments being used in many different locations, outside the
84 laboratory environment. It is suggested that this model transfer can be achieved through various
85 strategies including the combination of spectral data from multiple instruments in making a model
86 or through adjusting spectra to match a Primary (“Master”) instrument (A. D. Wang et al., 2019; Y.
87 D. Wang, Veltkamp, & Kowalski, 1991; Workman, 2018; Zhang, Li, Huang, Ni, & Ge, 2020).

88 Common approaches for the latter strategy include the application of Direct Standardisation (DS)
89 or Piecewise Direct Standardization (PDS) (Sun, Hsiung, & Smith, 2019; Workman, 2018).

90 It was hypothesised that a suitably sensitive method for the detection of food adulteration could
91 be developed using a single NIR device and chemometric modelling. It was further hypothesised
92 that this model could then be transferred to multiple devices to provide a means of rapidly
93 detecting food adulteration outside of a laboratory. In this study the development of chemometric
94 models for the detection of oregano adulteration, on a portable NIR device followed by their
95 validation and comparison against an ISO 17025 accredited FT-IR method is performed. Model
96 transferability was then investigated through a 27 participant, 22 country, international
97 interlaboratory study where several standardisation protocols were compared to determine which
98 would perform best in a real-world scenario.

99 2 Material and Methods

100 2.1 Instrumentation

101 SCiO (Model CP-SCM001), from Consumer Physics, is a handheld NIR spectrometer (68 x 40 x
102 19mm) weighing 35g that measures reflectance of samples in the wavelength range 740-1070nm.
103 It uses Bluetooth to connect to a smartphone or tablet and the SCiO Lab mobile app which in turn
104 uses the device's internet connectivity for two-way communication with 'The Lab', Consumer
105 Physics cloud-based software platform. The SCiO instrument allows for static measurements in
106 less than 5 seconds.

107 2.2 Software

108 2.2.1 'The Lab'

109 'The Lab' is the cloud-based software platform used directly with the SCiO. It is used to store SCiO
110 spectral scans in databases where (i) spectral data can be analysed and processed; (ii)
111 chemometric models can be created using Consumer Physics proprietary algorithms; (iii) model

112 performance can be tested. By using a researcher license, spectral data can be exported as a CSV
113 file for use in other software environments.

114 2.2.2 SIMCA 15

115 SIMCA 15 is standalone software from Sartorius Stedim, that allows for the selection of different
116 pre-processing variables and the generation of chemometric models and their testing using
117 classification algorithms that are not available in 'The Lab'.

118 2.2.3 PLS Toolbox/Matlab®

119 PLS Toolbox is an add-on from Eigenvector Research Incorporated for Matlab®. It provides a suite
120 of multivariate and machine learning tools for chemometric applications within Matlab®. It
121 provides a user interface for over 300 tools. Amongst other things, it allows for instrument
122 standardisation through multiple functions including DS and PDS
123 (EigenvectorResearchIncorporated, 2020).

124 2.3 Sample collection

125 In total 413 individual samples were used in this study.

126 Samples of oregano ($n=186$), with full provenance and traceability, as well as a number of samples
127 of previously identified adulterants (olive leaves ($n=10$), myrtle leaves ($n=7$), sumac leaves ($n=3$),
128 cistus leaves ($n=8$) and phlomis leaves ($n=2$)) were sourced from a number of supply chains and
129 used as a Reference set ($n=216$) to generate chemometric models.

130 A Validation set of samples ($n=197$) containing additional genuine oregano samples (with known
131 provenance) and commercially available oregano samples (obtained from various sources
132 including online retailers, convenience shops, supermarkets and marketplaces) were obtained
133 from multiple countries and used to test chemometric models. The Validation set consisted of

134 authentic oregano samples ($n=116$) and adulterated samples ($n=81$) with adulteration levels
135 greater than 13%, as determined by the FT-IR method (Black et al., 2016).

136 For the interlaboratory model transferability study, two genuine oregano samples and four
137 adulteratant samples, two cistus leaves and two olive leaves, were selected and distributed to
138 each of the 27 participants.

139 2.4 Spectral data acquisition

140 Samples were aliquoted into a 10 cm diameter glass petri dish, ensuring samples covered the base
141 and to a depth of at least 5mm when evenly distributed. Spectra were collected by placing the
142 instrument under the petri dish and scanning samples through the glass with the SCiOs optical
143 shade 'fixed-spacer' in position. This technique provides better spectral replication than
144 positioning the instrument on top of the sample (data not shown). All samples were scanned in
145 triplicate. Between each replicate the device was moved to a new location on the glass surface.
146 Replicate spectra were averaged to generate a single spectrum per sample per instrument. The
147 SCiO instrument was calibrated approximately every 10 minutes during data acquisition.

148 2.5 Development and evaluation of chemometric model performance

149 All samples were measured in a random order over several days on a single SCiO instrument
150 (Primary device (DF06170127)). Spectral data from the Reference set were used to generate both
151 binary (Oregano/Not Oregano) and multi-class (each leaf variety as an individual class) models.
152 Models were then tested using the independent Validation set and results compared to the FT-IR
153 method (Black et al., 2016).

154 2.5.1 'The Lab'

155 Once all scans were collected on the Primary device, 'The Lab' was used to filter and analyse data
156 before applying spectral pre-processing and building multiple chemometric models using the
157 provided tools and algorithms in expert mode.

158 Within expert mode, the user has freedom to choose between Log; Standard Normal Variate
159 (SNV); Subtract Average (-Avg); Subtract Minimum (-Min); Select Wavelength (WL); Select
160 Derivative (first derivative (1DER) and second derivative (2DER)); Wavelength Zscore (Zscore); and
161 Detrend pre-processing steps, as well as describing how to handle outliers. The user has the
162 freedom to select these processing steps in any order (except Log which can only be applied as the
163 first step or not at all), if at all, before creating the model. In total five of these processing steps
164 can be linked sequentially. At the time of writing only a Random Forrest (RF) algorithm was
165 available to generate classification models.

166 The output from creating a model is a confusion table of user defined class verses predicted
167 classification based on the cross-validation settings determined by the user. A performance value
168 (F1) is also returned. The optimal scenario would have no misclassification (a diagonal green line
169 with 100% in each cell) within the confusion table and $F1=1$.

170 Once models were created their performance was tested by predicting results for the Validation
171 set. A CSV file is produced giving predicted class. This was compared to known class and the
172 number of correctly identified samples determined.

173 2.5.2 SIMCA 15

174 Spectral data for the Primary device was exported from 'The lab' and replicate scans averaged in
175 Microsoft Excel before being imported into SIMCA 15. All spectral data where initially scaled to
176 Pareto Variance before multiple models created.

177 SIMCA 15 allows for several pre-processing techniques including derivatisation; Multiplicative
178 Scatter Correction (MSC); SNV; Savitzky-Golay smoothing (SG); and Exponentially Weighted
179 Moving Average (EWMA). These can be applied individually or sequentially as determined by the
180 user. Partial Least Squares – Discriminant Analysis (PLS-DA) and Orthogonal Partial Least Squares –
181 Discriminant Analysis (OPLS-DA) are two classification models provided in SIMCA 15.

182 Multiple models were created, and their performance tested by both internal cross-validation and
183 predicting results for the external Validation set. Internal cross-validation was evaluated using
184 $R^2X(\text{cumulative})$, $R^2Y(\text{cumulative})$ and $Q^2(\text{cumulative})$ values. Where $R^2X(\text{cumulative})$ is a
185 measure of the variation of the X block by all components within the model; $R^2Y(\text{cumulative})$ is a
186 measure of the variation of the Y block by all components within the model; and $Q^2(\text{cumulative})$ is
187 a measure of the total variation of the Y block that can be predicted by all components within the
188 model. Values closest to one are desirable. Within SIMCA 15 predicted results for the Validation
189 set are represented as a numerical value for each class in the model. The closer a value is to 1
190 indicates that sample is likely to belong to that class. Through using these values and assigning cut-
191 off values, below which samples are always considered adulterated, it was possible to present a
192 predicted class for each sample. These predicted classes were compared to known class and the
193 number of correctly identified samples determined for each model as a percentage correct
194 classification.

195 2.6 Interlaboratory study

196 An interlaboratory model transferability study was undertaken: Field-deployable Analytical
197 Methods to Assess the Authenticity, Safety and Quality of Food (Project Numbers D52040 and
198 G42007), coordinated by the International Atomic Energy Agency (IAEA). Thirty-two participants
199 representing twenty-two countries in Africa, Asia, Europe, North and South America as well as
200 Australia were invited to participate in this study. Participants ranged from having no spectroscopy

201 experience to substantial experience. The majority of participants were provided with a SCiO
202 instrument (unless they already owned a device) in addition to written and video instructions on
203 how to perform the analysis. These instructions duplicated the procedure in the Spectral data
204 acquisition section above; a glass petri dish for sample measurements; and 6 blind samples, 2
205 genuine oregano and 4 adulterants. Participants were asked to perform 2 main experiments,
206 obtain an authenticity result for each sample against the shared cloud based SCiO model; and
207 collect spectral data for evaluation against SIMCA 15 models. For this second task each participant
208 was required to analyse the six samples, collecting up to 21 scans per sample, with aliquots being
209 returned to their sample bag and thoroughly mixed between each measurement. Sample_01, _03
210 and _05 were analysed a total of seven times (in triplicate) on each instrument (to provide a
211 degree of noise cancelling when creating standardisation factors), while Sample_02, _04 and _06
212 where analysed three times (in triplicate) on each instrument giving a total of 30 unique sample
213 scans per device. Technical support was provided by Queen's University Belfast as needed.

214 Following on from direct predictions, where spectral data from individual devices were directly
215 predicted against the models created using the Primary device, several algorithms were
216 investigated that would standardise device spectral outputs to the Primary device.

217 2.6.1 Subtraction based standardisation

218 For each device, spectral data for each individual wavelength were averaged for Sample_01 ($n=21$
219 scans) creating a 1×331 matrix. For each device, this was subtracted from the spectral response for
220 that wavelength for Sample_01 on the Primary device thus providing a factor matrix to
221 standardise Sample_01. This process was repeated for each instrument for Sample_03 and
222 Sample_05. For each device, all three of these factor matrices where averaged, for each
223 wavelength, to yield a standardisation factor matrix (1×331) based on the three samples compared
224 to their spectral response on the Primary device. This standardised factor matrix was added to the

225 averaged spectral output for individual samples ($n=30$) for that device to create a new
226 standardised spectral output for that sample. Note, using this technique, each device utilises its
227 own unique 1×331 matrix to standardise its spectral output against the Primary device.

228 2.6.2 Division based standardisation

229 For each device, spectral data for each individual wavelength were averaged for Sample_01 ($n=21$
230 scans) creating a 1×331 matrix. For each device, and each wavelength, the Primary devices signal
231 was divided by this averaged spectral response per wavelength for Sample_01 thus providing a
232 factor matrix to standardise Sample_01. This process was repeated for each instrument for
233 Sample_03 and Sample_05. For each device, all three of these factor matrices were averaged, for
234 each wavelength, to yield a standardisation factor matrix (1×331) based on the three samples
235 compared to their spectral response on the Primary device. The averaged spectral output for each
236 sample ($n=30$) for each device was then multiplied by the appropriate factor matrix to create a
237 new standardised spectral output for that sample. Note, using this technique, each device utilises
238 its own unique 1×331 matrix to standardise its spectral output against the Primary device.

239 2.6.3 Direct Standardisation

240 PLS Toolbox was used to perform DS on the spectra from each device. With DS, spectra measured
241 on a Secondary device is corrected to match spectra measured on a Primary device. The response
242 matrices on both devices are related to each other by a transformation matrix that is created from
243 comparing the spectra for the same samples ran on both devices. The spectra of an unknown
244 sample measured on the Secondary ("Slave") device is standardised to that expected from the
245 Primary ("Master") device through application of the transformation matrix to the Secondary
246 ("Slave") device spectra (Y. D. Wang et al., 1991). Sample_01, _03 and _05, for device
247 DF06170127, were loaded as the Primary and the spectra for the same samples for each other
248 device was loaded in turn as the Secondary device. Each individual transformation matrix was then

249 applied to all the sample spectra from that Secondary device to create new standardised spectra
250 which were then imported into SIMCA 15 and used to generate predicted results for all samples.

251 2.6.4 Piecewise Direct Standardisation

252 PLS Toolbox was used to perform PDS on the spectra from each device. PDS maps spectral
253 responses from a Secondary (“Slave”) device to a Primary (“Master”) device (Sun et al., 2019). This
254 works by determining a structured standardisation matrix using spectra from samples that have
255 been scanned on both the Primary and Secondary device. This standardisation matrix is then used
256 to transform any spectrum from the Secondary device to the Primary device.

257 In PLS Toolbox, the spectra for Sample_01, _03 and _05, for device DF06170127, were loaded as
258 the Primary and the spectra for the same samples for each other device was loaded in turn as the
259 Secondary device. No pre-processing, SNV and mean centring were each used independently on
260 the data sets alongside applying 18 different window sizes (the number of spectral points
261 considered when constructing the standardisation matrix, ranging from 1 to 331 points in this
262 instance) to see which combination would yield the best predicted results. Each individual
263 standardisation matrix was then applied to all the sample spectra from that Secondary device to
264 create new standardised spectra which were then imported into SIMCA15 and used to generate
265 predicted results for all samples.

266 3 Results and discussion

267 3.1 Development and evaluation of chemometric model performance

268 3.1.1 ‘The Lab’

269 Using the spectra for the Reference set run on the Primary device, a total of 59 unique models
270 were created in ‘The Lab’, 29 multi-class and 30 binary models. Table 1 presents the two most

appropriate binary and multi-class models whilst data for all models are presented in supplementary material, Table ST-01. It can be observed that the binary model TheLabM34 has an $F1=0.99$ and correctly identified 100% of the authentic oregano samples, Table ST-01. However, this model only correctly identified 16% of the adulterated samples in the Validation set. Indeed, the worst performing model, in terms of correctly identifying genuine oregano, correctly identified 94.8% of the genuine oregano samples, however, in all instances the ability to correctly identify adulterated samples in the Validation set was low, Table ST-01. The best performing model, in terms of correctly identifying adulterated samples, can correctly identifying 32.1% of the adulterated samples in the Validation set, TheLabM48, Table 1. Typically, the method selected for use, if there is not one that correctly identifies all classes 100% of the time, would be one with a balanced performance *i.e.* best performing model for all classes. However, in this study there were no models that were evenly balanced in terms of correctly predicting authentic and adulterated samples, Table ST-01. Therefore, it was decided to use TheLabM48, Figure 1, in the model transferability study because it was the model that identified most adulterated samples and maintained over 97% correctly identified oregano samples in the Validation set.

There was a clear mismatch in performance between the internal cross-validation and predicting the external Validation set. In Figure 1 only 7% of the non-oregano samples were misclassified as genuine oregano whilst it was approximately 68% for the Validation set using model TheLabM48. The reason for this could be that all models were built using 100% oregano and adulterants whilst the Validation set is made up of retail samples with adulteration levels ranging from 10% upwards and the model is not sensitive enough to correctly identify adulteration at low levels. The RF algorithm is also known to work best when the number of samples in classes are balanced and this is clearly not the case in this instance with the reference set being made up of 186 genuine oregano samples and 30 adulterants. It is entirely possible that the RF model is biased towards

295 predicting samples as genuine oregano. Due to the poor performance of the RF algorithm, it was
296 decided to investigate alternative chemometric models in SIMCA 15.

297 3.1.2 SIMCA 15

298 Using the same spectral data, 26 unique models were built, 14 binary models and 12 multi-class
299 models. Table 2 presents the two most appropriate binary and multi-class models. Figure SF-01 (in
300 supplementary Information) provides the 2D score plots. Data for all models are presented in
301 supplementary material, Table ST-02. Table 2 and Table ST-02 lists both the internal cross-
302 validation statistics and the percentage correctly identified genuine oregano and adulterated
303 samples in the external Validation set. Supplementary Figure SF-02a represents the spectral
304 overlay of two oregano samples and several adulterants on both the FT-IR and NIR devices, whilst
305 SF-02b zooms in to the NIR (note this figure does not capture the complexity caused by variation
306 between samples). The percentage correctly identified adulterated samples was much higher than
307 that obtained for 'The Lab' across all models with the worst performing model correctly identifying
308 63.8% of the adulterated samples, SIMCA15_M19 which was an OPLS-DA binary model that used
309 1DER and EWMA pre-processing, Table ST-02. Based on the results for the external Validation set,
310 SIMCA15_M02 (a multi-class PLS-DA model with no additional pre-processing) gave the highest
311 correctly identified oregano results (87.8%), while SIMCA15_M27 (a multi-class PLS-DA model with
312 EWMA pre-processing) gave the highest correctly identified adulterated samples (88.8%), Table 2
313 and Table ST-02. In both instances the other correctly identified parameter remained high,
314 correctly identified adulterated samples (85.0%) for SIMCA15_M02 and correctly identified
315 oregano (86.1%) for SIMCA15_M27. Looking at R2X(cumulative) and Q2(cumulative), both internal
316 cross-validation statistics, these values are not particularly high when compared to the other
317 models in the table, Table ST-02. This could be because PLS-DA and OPLS-DA lend themselves best
318 to binary models where average R2X(cumulative), R2Y(cumulative) and Q2(cumulative) were

0.949, 0.819 and 0.767 respectively. When comparing the internal cross-validation statistics to the external Validation set results for SIMCA15_M02 and SIMCA15_M27 there was a clear miss-match in expected performance with the Validation set results being higher than expected based on the internal cross-validation. This may well be explained through the fact that they are multi-class models and the lower Q2(cumulative) may be indicative of the models inability to distinguish between all adulterants but being able to distinguish between the oregano class and the other classes as a group.

It is not a straightforward process to identify the variables that contribute to the separation of the clusters for SIMCA15_M02 and SIMCA15_M27 since these are multiclass models. Reviewing the Variable Influence on Projection (VIP) plot would indicate that the most influential wavelengths would appear to be related to protein and oil content.

3.2 Interlaboratory study on model transferability between instruments

Of the 32 invited participants 27 returned results. However, several of these participants returned results for multiple SCiO devices therefore, in total, results were returned for 34 unique SCiO devices.

3.2.1 Predicted results from 'The Lab' model

Each participant analysed the samples using the [test model] function within 'The Lab' phone-based app from Consumer Physics. Samples were predicted against model TheLabM48. Predicted results were provided directly on the end users phone/ipad screen after triplicate measurements. Scans performed in this way are not retained in Consumer Physics database. End Users were asked to record displayed results in a spreadsheet against the unique sample number and return the completed spreadsheet. Table 3 presents the results obtained by each participant. In total 18 devices (52.0%) returned the correct results for all six samples; 15 devices (44.1%) returned the

342 correct result for five samples while 1 instrument correctly identified only 4 samples. 33
343 instruments returned the correct answer for five of the six samples. Of the 15 instruments that
344 correctly identified five samples, 14 of them reported the same sample, Sample_06, incorrectly.
345 This sample contained olive leaves, thus was a known adulterated sample. The fact that these
346 instruments have predicted this sample as authentic oregano is a problem for routine analysis
347 because this would allow an adulterated material to be released into a supply chain. It would be
348 preferential that if there was a misclassification, it would be that an authentic oregano sample was
349 predicted as adulterated. In this instance, the sample would be sent for confirmation using more
350 sophisticated, laboratory based testing where the false result could be identified and the material
351 could be released, with some delay, as described previously (Wielogorska et al., 2018).

352 3.2.2 Predicted results from SIMCA 15 models

353 Each participant collected spectral data for the six anonymised samples. All samples were scanned
354 in triplicate for averaging. In addition, samples were replaced and mixed in their sample bags
355 before being reanalysed in the same manner. Samples_02, _04 and _06 were analysed a further
356 two times while Samples_01, _03 and _05 were analysed a further 6 times. This was to allow for
357 development of a correction factor based on the scans of these samples. Therefore, in total, each
358 instrument predicted 30 results.

359 3.2.2.1 Direct prediction

360 Spectral data was downloaded and predicted directly against SIMCA15_M02 and SIMCA15_M27
361 models using the same parameters as those elucidated during initial model development and
362 validation. Table 4 summarises the findings for all thirty-four instruments. For both models, 5
363 devices (14.7%) correctly predicted the results for all samples tested, while 13 devices (38.2%)
364 correctly predicted the results for five samples. Samples_01, _04 and _06 were correctly
365 predicted every time, while Sample _02 was misclassified once out of 102 predictions. Only 18

366 devices correctly predicted Sample_03 (Oregano) every time it was tested whilst this dropped to
367 six devices for Sample _05 (Oregano). Of the thirteen devices that correctly predicted five samples,
368 12 misclassified at least one scan of Sample_05. Interestingly this included the Primary device
369 which predicted the wrong result for Sample_05 two out of seven times. Comparing the models
370 from 'The Lab' software and SIMCA 15, 33 devices (97.1%) correctly identified five out of six
371 samples using the model in 'The Lab' software. This dropped to 18 devices (52.9%) for SIMCA 15
372 models. Furthermore, Sample_06 (Not Oregano), which was the problem sample in 'The Lab'
373 models was correctly predicted every time in the SIMCA 15 models. Sample_05 (Oregano) became
374 the problem sample. In many ways this is a preferable scenario because all adulterated samples
375 where correctly classified in the SIMCA 15 models and the false result for Sample_05 would be
376 picked up using confirmation analysis. However, the problem remains that only 18 devices could
377 correctly predict at least five out of six samples every time by directly predicting results from
378 multiple instruments. The next step was to see if this could be improved through instrument
379 standardisation.

380 *3.2.2.2 Predictions following subtraction-based standardisation*

381 Table 4 summarises the predictions for all 34 devices after a subtraction-based standardisation
382 factor was applied to the spectral output for each individual device. Similar results were obtained
383 for both tested models. Four out of six samples, Samples_01 (Not Oregano); _02 (Not Oregano);
384 _04 (Not Oregano); and _06 (Not Oregano) were correctly identified every time they were
385 measured ($n=238$ for Sample_01, $n=102$ for each of the other three samples). In both instances
386 two devices correctly predicted all six samples whilst 31 (including the Primary instrument)
387 correctly predicted five samples. Therefore 33 (97.1%) of the devices correctly predicted at least
388 five samples correctly every time they were analysed. Sample_05 (Oregano) remained the sample
389 that provided the most false results, including for the Primary device. Sample_03 (Oregano) was

misclassified all seven times by PAR14 (device DF0916008A). However, this is an older version (v1.1) of the SCiO instrument and we had been informed that models were not backwards compatible. Nevertheless, this device correctly predicted five of the six samples. PAR20 (DF341700CC) correctly predicted Sample_03 (Oregano) five out of seven times for both SIMCA 15 models. Overall, genuine oregano tests ($n=476$) were correctly predicted 76.5% of the time for SIMCA15_M02 and 73.5% of the time for SIMCA15_M27, with Sample_05 causing the decrease in value. Both instruments correctly predicted all adulterated sample tests ($n=544$) 100% of the time. Comparing the results for subtraction-based standardisation to direct prediction, Table 4, it is clear that using the subtraction-based standardisation factor has greatly increased the number of devices that correctly predicted at least five out of six samples, from 52.9% for direct prediction of each devices spectral output to 97.1% prediction after spectral standardisation using a subtraction-based factor, Table 4.

3.2.2.3 Predictions following division-based standardisation

Table 4 summarises the predictions for all 34 devices after a division-based standardisation factor was applied to the spectral output for each individual device. The findings are broadly in line with those of the subtraction-based standardisation. The main differences being that using the division-based factor, PAR14 (device DF0916008A) correctly predicts Sample_03 twice instead of no correct predictions for both models; PAR20 (device DF341700CC) correctly predicts Sample_03 in six instead of five tests of Sample_03 in SIMCA15_M02; and for SIMCA15_M27, PAR31 (device DF341700J6) predicts four out of six samples correctly every time ($n=30$). This device misclassified Sample_01 once out of seven tests and Sample_05 four out of seven tests. Overall, the correctly identified oregano ($n=476$) is slightly higher, 77.7% for the division-based correction factor using SIMCA15_M02 than for the subtraction-based correction factor (76.5%).

413 3.2.2.4 Predictions following Direct Standardisation

414 Compared to the direct prediction, subtraction-based and division-based standardisation, DS has
415 performed poorly with only eight devices being able to correctly predict at least 5 out of six
416 samples every time they were ran ($n=30$ per device), Table ST-03. PAR31 (device DF341700J6)
417 misclassified Sample_03 once out of seven tests otherwise this would have also been correctly
418 classified 100% of the time ($n=238$) on all devices.

419 3.2.2.5 Predictions following Piecewise direct standardisation

420 Applying pre-processing (SNV and mean centring) before PDS had a detrimental effect on model
421 performance (data not shown). Table ST-04 provides a summary of results for devices ($n=34$) that
422 were able to achieve at least five out of six correctly predicted results 100% of the time after the
423 appropriate PDS (no pre-processing) and various window sizes matrix were applied to spectra and
424 tested against the SIMCA 15 models SIMCA15_M02 and SIMCA15_M27. As can be seen PDS
425 corrected spectra with 1-point and 3-point windows were the only two conditions that showed
426 every device getting at least five out of six samples correct every time they were tested ($n=30$ per
427 device). Table 4 shows that PDS (window 01 and window 03) allowed for devices to correctly
428 identify the adulterated samples every time they were tested on every device ($n=544$). For both,
429 Sample_03 (Oregano) is correctly identified 98.8% of the time. Further in-depth analysis of these
430 results showed that only PAR14 (device DF0916008A) misclassified this sample, four times out of
431 its seven analyses. This device is an older version (version 1.1) of the SCiO and the models were
432 not expected to be backward compatible with this device, which incidentally correctly classified
433 five out of six samples every time they were tested in it. All 33 version 1.2 devices correctly
434 classified five out of six samples every time. As with the previous results above, Sample_05
435 (Oregano) remained the sample that was misclassified the most.

436 3.3 Sample_05

437 It is clear from the results presented that Sample_05 has been an issue. The models were created
438 and validated several months before the transferability trial was performed. Figure 2a and Figure
439 2b shows an overlay plot of the original scan of Sample_05 (black line) and the additional scans
440 carried out as part of the transferability interlaboratory study when no processing and EWMA
441 processing has been applied. The original scan sits below the cluster of other scans in both
442 instances. When SNV was applied to all the spectra the original scan appears to fit with the other
443 spectra, Figure 2c. For this reason, all the standardised spectra were tested against models
444 (SIMCA15_M05; SIMCA15_M11; SIMCA15_M12; SIMCA15_M13; and SIMCA15_M15, as presented
445 in Table ST-02) which all contain SNV correction, and results predicted. Note, SIMCA 15
446 automatically applies the same pre-processing to the Validation set as had been applied to the
447 Reference set when generating the model. With several iterations comparable results were
448 obtained, all 34 devices correctly identifying 100% of the scans ($n=30$ per device) of five out of six
449 samples. However, none of the standardisation techniques were able to increase the number of
450 instances when all scans ($n=30$ per device) of six out of six samples were correctly predicted (data
451 not shown). Sample_05 remained an outlier in this study. It is possible that it may have perished in
452 storage or may have suffered cross-contamination before being aliquoted for the interlaboratory
453 study.

454 4 Conclusion

455 Comparing the results for SIMCA 15 models for direct prediction, subtraction-based
456 standardisation, division-based standardisation, Direct Standardisation, and Piecewise Direct
457 Standardisation, not all methods were equal. Deployment of a model across multiple SCiO devices
458 is not possible when directly predicting results against a model developed on one Primary SCiO
459 device. Only 18 out of 34 devices were able to predict the correct result every time the samples

460 were tested ($n=30$ per device) for five samples out of six. This indicates that some form of device
461 standardisation should be considered to improve results across devices. In this instance Direct
462 Standardisation is not suitable, performing worse than direct measurements, with only eight of 34
463 devices being able to predict five out of six samples correctly every time they were run. Using a
464 subtraction-based or a division-based standardisation improved this figure to 33 out of 34. Using
465 Piecewise Direct Standardisation, either with a 1-point or 3-point window, allowed for all devices
466 to correctly predict five of six samples every time they were run ($n=30$ per device). It is improbable
467 that any Secondary device will perform better than the Primary device therefore having all
468 instruments being able to predict five out of six samples every time they were run was the best
469 outcome achievable in this instance. When comparing the two SIMCA 15 models (SIMCA15_M02
470 and SIMCA15_M27) their performance were comparable within the standardisation method
471 applied. When considering authentic and adulterated sample sets individually across the 34
472 devices, the direct prediction of overall authentic samples is 54.8% (with the inclusion of
473 Samlpe_05) whereas with subtraction-based standardization and division-based standardization
474 the prediction is around 76 and 77 % respectively. The direct prediction of overall adulterated
475 samples is 99.8% whereas with subtraction-based standardization and division-based
476 standardization the prediction is around 100 and 100 % respectively.

477 Direct predictions using 'The Lab' software performed well with 33 of 34 devices correctly
478 predicting five of the six samples correctly. However, closer examination of the results show that
479 preferentially a SIMCA 15 model with PDS (window 01 or 03) would be the method of choice. Not
480 only because more devices get the correct answer but also because the problem sample for 'The
481 Lab' software is an adulterated sample being misclassified as genuine while it is the other way
482 around for the SIMCA 15 models. Retaining stock and sending a sample for confirmation to
483 discover if the material is genuine is more preferential than having to recall product after later

484 discovering that a material is adulterated. This study used a Primary/Secondary instrument
485 approach to address model transferability. An alternative method would be to generate models
486 based on spectra from multiple devices with the aim of covering device variability within the
487 model. This would be a labour-intensive approach requiring Reference set samples to be scanned
488 on multiple instruments.

489 This study supports the hypothesis that a suitable method for food authenticity testing can be
490 developed using a single NIR device and chemometric models. Furthermore, using appropriate
491 standardisation techniques, this model can be transferred across multiple devices.

492 Using device standardisation, it is possible to transfer a single device model for oregano
493 authenticity across 34 devices that have been tested by individuals, with varying degrees of
494 expertise, who are based in different locations around the world. It also demonstrates that such
495 devices, when made in a user-friendly manner, can be deployed with minimal training and
496 support. In this instance there was need for manual intervention with the SIMCA 15 models,
497 however this manual processing can be overcome through appropriate proprietary software
498 programming.

499 This study has, for the first time, examined the ability to use a low-cost field deployable NIR device
500 coupled to chemometrics, across five continents, to detect adulterated food. The results are
501 encouraging and warrant further studies with additional sample sets, covering a wider range of
502 adulterants and concentrations to fully ascertain how robust the devices/ models / standardisation
503 approaches are. In a real-world scenario, the authors would anticipate that the device and models
504 should only be used as a screening tool where both adulterated samples and random samples
505 should be sent for confirmation in a laboratory. The current instrument and software setup of the
506 SCiO device meets the needs of researchers by allowing the development and validation of models
507 both on the platform and offline. However to make this a truly portable solution that facilitates

508 routine analysis by multiple end users of varying skill levels, the range of classification algorithms
509 and pre-processing steps available in “The Lab” software would need to be increased to include at
510 least those available in SIMCA 15 as well as giving researchers flexibility to define parameters such
511 as cut-off levels. Furthermore, the software would need to allow for device standardisation as an
512 option. These functions do not necessarily need to be end user facing but are necessary for those
513 dedicated to developing globally applicable methods for routine analysis. The SCiO is one of many
514 microminiaturized instruments currently on the market and performance will be different across these
515 platforms, primarily because they are built with different specifications and the wavelengths covered are
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The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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610 Figures

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612 Figure 1: TheLabM48 model generated after averaging replicate spectra, applying Zscore pre-processing and RF
613 classification algorithm.

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Figure 2: Overlay of spectra for all Sample_05 samples ran on the Primary device a. No Processing; b. following EWMA processing; c. following SNV processing.

Model ID	Multi-class / Binary	Processing	F1	Correct ID Oregano (n=116)	Correct ID Adulterated (n=81)
TheLabM07	Multi-class	Log SNV -Avg 2DER	0.958	97.4%	23.5%
TheLabM09	Multi-class	Log SNV -Min 2DER	0.958	97.4%	23.5%
TheLabM48	Binary	ZScore	0.97	97.4%	32.1%
TheLabM59	Binary	WL750 - 1050 Zscore	0.974	99.1%	29.6%

618 Table 1: Multi-class and Binary models produced in ‘The Lab’. Details of pre-processing techniques applied to spectra,

619 F1 value and percentage correctly identified oregano and adulterated samples.

Model ID	Multi-class / Binary	Processing	Model Algorithm	R2X (cumulative)	R2Y (cumulative)	Q2 (cumulative)	Cut-off	Correct ID Oregano (n=116)	Correct ID Adulterated (n=81)
Simca15_M02	Multi-class	unprocessed	PLS-DA	1	0.523	0.355	0.81	87.8%	85.0%
Simca15_M08	Binary	unprocessed	PLS-DA	1	0.809	0.72	0.84	85.2%	87.5%
Simca15_M23	Binary	EWMA	PLS-DA	1	0.808	0.725	0.82	87.0%	85.0%
Simca15_M27	Multi-class	EWMA	PLS-DA	1	0.522	0.355	0.82	86.1%	88.8%

Table 2: Multi-class and Binary models produced in SIMCA 15. Details of pre-processing techniques applied to spectra, internal cross-validation statistics and predicted results for the external Validation set.

Participant ID	Instrument ID	Sample_01 (Not Oregano)	Sample_02 (Not Oregano)	Sample_03 (Oregano)	Sample_04 (Not Oregano)	Sample_05 (Oregano)	Sample_06 (Not Oregano)	Number of correct Results
PAR01	DF511601CP	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR02	DF06170196	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR03	DF3217008A	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR05	DF341700HR	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR06	DF061701JM	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR07	DF061701V3	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR08	DF0617013W	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR10	DF061701JX	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR11	DF341700EZ	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR12	DF341700AF	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR14	DF0916008A	Not Oregano	Not Oregano	Oregano	Not Oregano	Not Oregano	Not Oregano	5/6
PAR17	DF341400GF	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR18	DF341700CL	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR19	DF3417009Y	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR20	DF341700CC	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR21	DF341700B2	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR22	DF321700AQ	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR23	DF341700HQ	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR24	DF341700J8	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR25	DF341700G0	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR26	DF341700A5	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR27	DF34170038	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR28	DF511600JF	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR29	DF06170127	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR29	DF061701TX	Not Oregano	Not Oregano	Oregano	Oregano	Oregano	Oregano	4/6
PAR29	DF061701UZ	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR29	DF341700C2	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR30	DF341700HN	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR31	DF341700J6	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6

PAR32	DF06170102	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Oregano	5/6
PAR32	DF3417009S	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR32	DF4516004Z	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR32	DF481601EC	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6
PAR32	DF261700DY	Not Oregano	Not Oregano	Oregano	Not Oregano	Oregano	Not Oregano	6/6

622 *Table 3: Summary of all participants results obtained from the ‘test model’ function in ‘The Lab’ phone-based app.*

	Model	Sample_01 (Not Oregano) (n=238)	Sample_02 (Not Oregano) (n=102)	Sample_03 (Oregano) (n=238)	Sample_04 (Not Oregano) (n=102)	Sample_05 (Oregano) (n=238)	Sample_06 (Not Oregano) (n=102)	6/6 100% correct	5/6 100% correct	At least 5/6 100% correct	Overall Correct ID Oregano (n=476)	Overall Correct ID Not Oregano (n=544)
Direct prediction	SIMCA15_M02	100.00%	99.00%	66.80%	100.00%	42.90%	100.00%	5/34 (14.7%)	13/34 (38.2%)	18/34 (52.9%)	54.80%	99.80%
	SIMCA15_M27	100.00%	99.00%	64.70%	100.00%	40.30%	100.00%	5/34 (14.7%)	13/34 (38.2%)	18/34 (52.9%)	52.50%	99.80%
Subtraction based standardisation	SIMCA15_M02	100.00%	100.00%	96.20%	100.00%	56.70%	100.00%	2/34 (5.9%)	31/34 (91.2%)	32/34 (97.1%)	76.50%	100.00%
	SIMCA15_M27	100.00%	100.00%	96.20%	100.00%	50.80%	100.00%	2/34 (5.9%)	31/34 (91.2%)	33/34 (97.1%)	73.50%	100.00%
Division based standardisation	SIMCA15_M02	100.00%	100.00%	97.50%	100.00%	58.00%	100.00%	2/34 (5.9%)	31/34 (91.2%)	33/34 (97.1%)	77.70%	100.00%
	SIMCA15_M27	100.00%	100.00%	96.60%	100.00%	50.80%	100.00%	2/34 (5.9%)	30/34 (88.2%)	32/34 (94.1%)	73.70%	100.00%
PDS (Win01)	SIMCA15_M02	100.00%	100.00%	98.30%	100.00%	27.30%	100.00%	0/34 (0%)	34/34 (100%)	34/34 (100%)	62.80%	100.00%
	SIMCA15_M27	100.00%	100.00%	98.30%	100.00%	25.10%	100.00%	0/34 (0%)	34/34 (100%)	34/34 (100%)	61.70%	100.00%
PDS (Win03)	SIMCA15_M02	100.00%	100.00%	98.30%	100.00%	27.30%	100.00%	0/34 (0%)	34/34 (100%)	34/34 (100%)	62.80%	100.00%
	SIMCA15_M27	100.00%	100.00%	98.30%	100.00%	25.10%	100.00%	0/34 (0%)	34/34 (100%)	34/34 (100%)	61.70%	100.00%

623 Table 4: Summary of all participants results obtained from SIMCA15_M02 and SIMCA15_M27 models based on: direct prediction; applying the subtraction-based standardisation

624 factor; applying the division-based standardisation factor; and applying PDS (without pre-processing) with 1 point and 3 point window sizes. n values are the sum of observations of

625 replicated tests with 34 devices. The column labelled “At least 5/6 100% correct” is the sum of devices with either five or six samples 100% correct.