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Measuring the colour of virgin olive oils in a new colour scale 1 using a low-cost portable electronic device 2

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20 Abstract. The Modified Uniform Oil Colour Scale (MUOCS) is proposed for the colour 21 specification of virgin olive oils. MUOCS has 60 standard colours, the same number as 22 the two previous scales available for the same purpose: Uniform Oil Colour Scale 23 (UOCS) and Bromthymol Blue (BTB). A remarkable improvement in accuracy can be 24 achieved from MUOCS standards: For a broad dataset of 1700 virgin olive oils 25 produced in Spain during 4 different harvests, the average colour differences to the 26 closest standards were 2.86, 3.99, and 8.17 CIELAB units using MUOCS, UOCS and 27 BTB, respectively. A low-cost (<60 Euros) portable electronic device is proposed for 28 the colour specification of virgin olive oils based on MUOCS and BTB standards. This 29 device can operate with USB connection to a computer or AAA batteries, and is based 30 on fast (<0.25 s) transmittance measurements of the virgin-olive-oil sample placed in a 31 5-mm pathlength quartz cell. The device may avoid the use of expensive laboratory 32 instrumentation for colour measurement and can be easily employed by non-technician 33 users. For a reduced set of commercial virgin olive oils with random colours, the 34 MUOCS classifications provided by our device agreed with those given by conventional 35 spectrophotometric measurements in 92% of the cases.

- 38 Blue (BTB) method, Uniform Oil Color Scale (UOCS), DIN99, CIELAB.
- 39

³⁷ **Keywords:** Color of virgin olive oils, color-measurement instrumentation, Bromthymol

40 **1. Introduction**

Colour is an important property of many foods for two main reasons: its relationship 41 42 with other chemical and physical properties of food (which may be also related to 43 ripeness, processing techniques, storage conditions, etc.), and its strong influence in 44 consumers' preferences, which govern subsequent buying decisions. Accurate colour specification is often a key part of a complete food-quality control. As a current 45 46 example of the growing interest in food colour, the 2010 interim meeting of the 47 International Colour Association (AIC, 2010) focused on this topic under the title "Color and Food: From the Farm to the Table", with a total of 139 presentations from 48 49 researchers in 26 different countries.

50 Spain is the world's leading producer of olive oils (39.3% of global production in the 51 past 5 years), which are recognized as high-quality foods with many beneficial health 52 properties. Also olive-oil imports are increasing notably in many countries, e.g. 5-fold 53 in USA during the past 25 years (International Olive Council, 2011). Therefore, 54 production of the best virgin olive oils is economically important in Spain, and the 55 colour of virgin olive oils cannot be neglected. Oil colour strongly influences people's 56 preferences, as shown, for example, by the fact that professional olive-oil tasters use 57 tinted cups, because just colour perception of olive oils may strongly bias assessments 58 of other attributes (Izquierdo, 1997; Melgosa et al., 2009). Different researchers have 59 paid attention to colour specification of virgin olive oils, and this paper is a step forwards in this sense. 60

61 For the colour specification of virgin olive oils, researchers proposed the Bromthymol Blue (BTB) method (Gutiérrez & Gutiérrez, 1986), which was standardized in 1997 62 63 (AENOR, 1997). The BTB method proposes a subjective visual comparison between 64 the colour of a virgin-olive-oil sample and a two-dimensional scale with 60 (10x6) fixed solutions, called BTB standards, looking for the solution with the colour closest to the 65 66 sample. The BTB standards are not olive oils, but a mixture of specific chemical products producing a set of colours which are very similar to those of most virgin olive 67 oils. Appropriate transform equations from BTB to the CIELAB colour space (CIE, 68 69 2004) have been proposed (Moyano et al., 1999), bearing mind that BTB is a specific 70 olive-oil colour scale, while current international colour specifications by the 71 International Commission on Illumination recommend the use of CIELAB (or 72 CIELUV). However, further research has revealed limited precision and accuracy from 73 the BTB method (Melgosa et al., 2000), mainly for two reasons: the 60 BTB standards 74 are irregularly spread in an approximately uniform colour space similar to CIELAB, and 75 they do not cover the real colour gamut of virgin-olive-oil samples (specifically, those 76 with the most saturated yellow colours fall outside the gamut). In addition, it has been 77 also reported some lack of temporal colour stability of the 60 BTB standards during 2-3 78 months after their preparation (Melgosa et al., 2001).

79 In view of these flaws of the BTB method, together with the intrinsic subjective nature 80 of any visual colour comparison, a new colour scale for virgin olive oils, called the 81 Uniform Oil Colour Scales (UOCS) was proposed in 2004 (Melgosa et al., 2004). 82 UOCS has the same number of standards as BTB (i.e. 60) so that the two scales can be 83 meaningfully compared. However, the UOCS standards are not real solutions, but 84 theoretical points in a tridimensional colour space, in such a way that the UOCS method 85 is not based on a subjective visual comparison, as suggested by the BTB method. The UOCS method is objective, using a theoretical computation of the lowest colour 86

87 difference between the colour instrumentally measured for a virgin-olive-oil sample and 88 the set of colours specified by the 60 UOCS standards. It was found that, for a wide set 89 of 1700 virgin-olive-oil samples produced in Spain during four different harvests (Moyano, 2002), the UOCS improved the BTB scale by about a factor 2 (Melgosa et al., 90 91 2004). That is, the average colour differences between each of these 1700 samples and 92 their closest standards was about two-fold greater using the BTB standards than using 93 the UOCS standards. This good result of the UOCS also stood up when considering 94 virgin-olive-oil samples corresponding to different varieties, harvests, and degrees of 95 ripeness (Melgosa et al., 2005).

As mentioned above, while the 60 BTB standards are real physical samples, the 60 UOCS standards are a set of points in a colour space. Therefore, in practice, the use of the UOCS requires an instrumental colour measurement of the virgin-olive-oil sample in the laboratory, followed by computations of colour differences. That is, the use of the UOCS requires a colour-measurement instrument (e.g. a spectrophotometer) as well as some knowledge of colour science, which limits its practical application.

102 Several portable instruments for colour measurement have been developed by some of the authors of the present paper for different applications (Palma et al., 2008; Capitán-103 Vallvey & Palma, 2011; Martínez-Olmos et al., 2011). The prototypes developed have 104 105 shown both high reliability and technical specifications comparable to those in more 106 complex and expensive analytical laboratory instrumentation. One example of the advances in this field is a recent paper proposing the colour determination of red wine 107 by a compact instrument (De la Torre et al., 2009). In the present paper, we propose a 108 109 low-cost portable electronic device that can be used by people without any special 110 knowledge in colour science. This device provides the colour specification of a virgin-111 olive-oil sample in the earlier BTB scale and also in the Modified Uniform Oil Colour 112 Scale (MUOCS), a new colour scale for virgin olive oils which has been developed by 113 us after detecting flaws in the UOCS. Like UOCS, MUOCS is also a set of 60 points in 114 a colour space. The main characteristics of MUOCS are explained, showing that it achieves a noteworthy improvement with respect to the previous UOCS and BTB scale. 115 116 Properly, the electronic device we have designed cannot be called a colorimeter, 117 because its goal is not to measure a colour in a selected colour space (e.g. CIELAB or DIN99d), but rather to find simply which of the 60 BTB or MUOCS standards has the 118 119 closest colour to the one of a given virgin-olive-oil sample.

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121 **2. Materials and Methods**

Two different parts can be distinguished in the current paper: A) The introduction of the Modified Uniform Oil Colour Scale (MUOCS); B) the development and performance of the electronic device we designed to measure MUOCS and BTB colours of a virginolive-oil sample. Here we briefly mention the main materials and methods employed in each one of these two parts, which are detailed in the "Results and Discussion" section. Specifically:

A.1) Colours of a set of 1700 virgin-olive-oil samples (Moyano, 2002) were measured
with a Hewlett-Packard 8452 UV-visible spectrophotometer using quartz cells with a 5mm pathlength, assuming D65 illuminant and CIE 1964 standard colorimetric observer.
The 60 MUOCS standards were defined from this set of virgin olive oils, considering a
regular rhombohedral lattice like the one employed by the Uniform Color Scales of the

Optical Society of America (MacAdam, 1974) in the DIN99d (Cui et al., 2002) colourspace.

A.2) Flaws found in the development of previous BTB (Gutiérrez & Gutiérrez, 1986) 135 136 and UOCS standards (Melgosa et al. 2004) which led us to the current proposal of the MUOCS standards are described. The improvements achieved by MUOCS upon UOCS 137 and BTB are shown by different methods: plots showing the regularity of the spread of 138 139 the different sets of standards in the DIN99d colour space; percentage of 1700 virgin-140 olive oil samples classified by each one of the standards; average and standard deviation 141 of CIELAB colour differences between each one of the 1700 virgin-olive-oil samples 142 and their closest standards in BTB, UOCS and MUOCS.

143 B.1) Components of the electronic device we designed to measure the BTB and 144 MUOCS colours of a given virgin-olive-oil sample are illustrated in a block diagram. 145 The characteristics of the NSPW300 white LED source (Nichia Japan), S9706 colour 146 sensor (Hamamatsu Photonics, Japan), PIC18F2550 microcontroller (Microchip 147 Technology Inc., USA), and supplementary 25LC1024 EEPROM memory (Microchip 148 Technology Inc., USA) used in the design of our device are described. A software 149 application in Visual Basic 2008 (Microsoft Corp., Redmond, WA, USA) was developed for proper work of this instrument, which includes two optional operating 150 151 modes: portable (AAA batteries) and USB connection to a computer.

152 B.2) The practical operation with our instrument is described step by step, considering 153 the preliminary measurements of black and white signals, as well as the corresponding 154 manipulation of measured RGB signals of a virgin-olive-oil sample. The calibration 155 procedure employed in our device is described. Our calibration is based on experimental 156 measurements performed with a JASCO-V650 spectrophotometer (5-mm pathlength 157 quartz cells) for a set of 10-ml solutions of each one of the 60 BTB standards (Gutiérrez 158 & Gutiérrez, 1986), and the application of the pseudo-inverse method (Moore, 1920; 159 Penrose, 1955). To test the accuracy achieved by our electronic device measuring MUOCS colour, we employed a set of 37 commercial virgin-olive-oils with random 160 161 colours.

162 Detailed descriptions of all items previously mentioned are given in the next section.

163

164 **3. Results and Discussion**

165

166 **3.1. The Modified Uniform Oil Colour Scale (MUOCS)**

The following characteristics are common to the UOCS and MUOCS methods: 1) They 167 are objective (non-visual) methods for the colour specification of a virgin-olive-oil 168 sample in specific scales, from the lowest colour difference between the colour of the 169 170 sample and a fixed set of 60 colours, called standards, which define the corresponding scales. 2) They are based on a unique set of 1700 virgin-olive-oil samples (Moyano, 171 172 2002), which can be considered highly representative of the whole colour range of virgin olive oils available in Spain. 3) The colours of these 1700 samples were 173 174 represented and analysed in the DIN99d colour space (Cui et al., 2002), which is a modern CIELAB-based colour space with improved uniformity over CIELAB. 175 176 Equations defining the DIN99d colour space from CIELAB are provided in Appendix

177 A. Seeking uniform sampling of the region of colour space where the 1700 samples are 178 positioned (i.e. the greatest possibility of achieving a near match between colours of 179 virgin-olive-oil samples and the set of 60 standards), the UOCS and MUCOS standards 180 were placed in the DIN99d space following a regular rhombohedral (cubo-octahedron) 181 lattice (Wyszecki, 1954), like the one employed by the Uniform Color Scales of the Optical Society of America (MacAdam, 1974; Judd & Wyszecki, 1975; Luke 1999). 182 This lattice is a type of "closest packing", where each of the standards is surrounded by 183 184 12 equidistant nearest neighbours, this distance being called the lattice constant.

185 However, some flaws have been detected in UOCS, leading us to the current proposal of MUOCS. Firstly, it should be mentioned that the original 1700 virgin-olive-oil 186 187 samples (Moyano, 2002) were measured with a Hewlett-Packard 8452 UV-visible spectrophotometer using quartz cells with a 5-mm pathlength, and the measured spectral 188 189 transmittances were converted to a 10-mm pathlength while assuming the Bouguer-Lambert-Beer law, before computation of colour coordinates leading to the UOCS 190 191 standards. However, for a set of virgin-olive-oil samples, it has been found that the 192 assumption of the Bouguer-Lambert-Beer law between 5 and 10 mm pathlengths led to 193 significant errors, causing considerable differences (3.6 CIELAB units on the average) 194 with respect to the experimental measurements (Gómez-Robledo et al., 2011). 195 Accordingly, it was concluded that it was better to keep original measurements at 5-mm 196 pathlengths for the development of the MUOCS standards. Adoption of cells with 5-mm 197 pathlength for colour measurements of virgin olive oils has also been recommended for 198 other practical reasons (Gómez-Robledo et al., 2011). Secondly, the algorithms 199 designed to develop the UOCS and MUOCS were slightly different, in such a way that 200 some discontinuities found in the lattice corresponding to the UOCS standards have been solved by MUOCS standards (Gómez-Robledo, 2011). The aforementioned 201 202 algorithms start from the centre of gravity of the 1700 virgin-olive-oil-samples in DIN99d and proceed by calculating a lattice with constant 3.0 units. In the case of 203 204 UOCS, successive planes or layers were computed, and finally any standards that 205 classified a low number of oil samples were removed by visual inspection to achieve the desired number of 60 standards. In the case of MUOCS, from the centre of gravity of 206 207 the 1700 samples in DIN99d, successive sets of 12 nearest neighbours were computed 208 at a time, checking that distances of any new standards to the set of 1700 samples never exceeded 7.0 DIN99d units. In this way, final visual inspection to achieve the 60 209 210 MUOCS standards was easier and discontinuities in the lattice were avoided.

211 Figure 1 shows the BTB, UOCS, and MUOCS standards together with the 1700 virgin 212 olive oils in the three planes of the DIN99d colour space. It can be noted that BTB 213 standards are not at all regularly spread in DIN99d colour space, and colours of many 214 oil samples with high b_{99d} and L_{99d} values lie outside the gamut provided by the BTB 215 standards. As expected, it is also noticeable that the MUOCS and UOCS standards 216 follow a similar geometrical spread of their standards. However, the MUOCS standards 217 offer improvements over the UOCS in a double sense: they made a better fit with the 218 cloud of points representing the 1700 oil samples, and they were more regularly and 219 continuously distributed in the colour space. In fact, it was computed that the average 220 distances between the 1700 virgin-olive-oil samples and their corresponding nearest 221 standards were 8.17, 3.99, and 2.86 CIELAB units (with standard deviations of 6.64, 222 3.05, and 1.43 CIELAB units, respectively) for the BTB, UOCS, and MUOCS 223 standards, respectively. This result clearly indicates that UOCS exceeded BTB in 224 accuracy by about a factor 2, as reported before (Melgosa et al., 2004), and also that current MUOCS standards provide an additional remarkable improvement with respect 225

- to UOCS standards: an average reduction of colour differences of more than 25%,
- together with a reduction of the standard deviations of more than 50%.



Figure 1. Colour coordinates of 1700 virgin-olive-oil samples¹² measured at 5-mm pathlength, together with the 60 BTB (also 5-mm pathlength), UOCS, and MUOCS standards, in the three planes (a_{99d}-b_{99d} top, a_{99d}-L_{99d} middle, b_{99d}-L_{99d} bottom) of the DIN99d (Cui et al., 2002) colour space.

As further proof of the improvement of MUOCS over UOCS and BTB, Figure 2 shows the number of oil samples classified by the 60 standards in each of these three colour 235 scales. It can be seen that, while BTB standard number 10 (with BTB code 2/10) 236 classified about 850 oil samples, many other BTB standards classified almost zero oil 237 samples, this being a clearly unacceptable result. The situation clearly improves for the 238 UOCS standards, and even more for the MUOCS standards, which all classified 239 between 5 and 110 oil samples from the original dataset of 1700 virgin-olive-oil 240 samples. Finally, Figure 3 shows the percentage of the 1700 oil samples classified by BTB, UOCS, and MUOCS standards using different tolerances (CIELAB units). Once 241 242 again we see the pronounced improvement over BTB achieved by both UOCS and 243 MUOCS for any tolerance level, as well the improvement of MUOCS over UOCS.



Figure 2. From our dataset of 1700 virgin-olive-oil samples (Moyano, 2002), the number of samples classified by each one of the 60 standards provided by BTB (up), UOCS (medium), and MUOCS (bottom).



Figure 3. Percentage of 1700 virgin-olive-oil samples (Moyano, 2002) classified with a tolerance level of *X* CIELAB units using BTB, UOCS and MUOCS standards.

251 A three-number code was adopted to design each of the 60 MUOCS standards in an 252 intuitive way, as indicated in Table 1. The first number of the code ranges from 1 to 14 253 and indicates increasing lightness values. The second number is always an even number 254 ranging from 2 to 16, and increasing values indicate displacement of the colour of the 255 standards towards green hues. Finally, the third number ranges from 1 to 14, increasing values indicating displacements towards yellow hues. The specific codes and DIN99d 256 257 coordinates of the 60 MUOCS standards are provided in Appendix B. In the 258 rhombohedral (cubo-octahedron) lattice conducting to MUOCS standards, each 259 standard is surrounded by 12 equidistant nearest neighbours in the DIN99d space. 260 However, the distances between contiguous L99d, a99d, and b99d planes is not constant but 1.50, 0.86, and 2.45 DIN99d units, respectively, as shown in Table 1. 261

Table 1. DIN99d values corresponding to the three-number code employed to designate
 the MUOCS standards.

| Lightness | L _{99d} | Green Hue | <i>a</i> _{99d} | Yellow Hue | b _{99d} |
|-----------|------------------|-----------|-------------------------|------------|-------------------------|
| 1 | 78.39 | 2 | 6.14 | 1 | 14.26 |
| 2 | 79.89 | 4 | 5.27 | 2 | 16.71 |
| 3 | 81.39 | 6 | 4.41 | 3 | 19.16 |
| 5 | 84.39 | 8 | 3.54 | 4 | 21.61 |
| 4 | 82.89 | 10 | 2.67 | 5 | 24.06 |
| 6 | 85.89 | 12 | 1.81 | 6 | 26.51 |
| 7 | 87.39 | 14 | 0.94 | 7 | 28.96 |
| 8 | 88.89 | 16 | 0.08 | 8 | 31.41 |
| 9 | 90.39 | - | - | 9 | 33.86 |

| 10 | 91.89 | - | - | 10 | 36.31 |
|----|-------|---|---|----|-------|
| 11 | 93.39 | - | - | 11 | 38.76 |
| 12 | 94.89 | - | - | 12 | 41.21 |
| 13 | 96.39 | - | - | 13 | 43.66 |
| 14 | 97.89 | - | - | 14 | 46.11 |

266

3.2. Electronic device measuring MUOCS and BTB colours

The block diagram of the portable instrument developed (Carvajal Rodríguez et al., 268 269 2011) is presented in Figure 4. The current estimated cost of all the components 270 comprising this instrument (quartz cell excluded) is below 60 Euros (Fernández Salmerón, 2011). Briefly, the prototype computes the closest MUOCS and BTB 271 272 standards to a given olive-oil sample by measuring its transmitted light. To do so, in the 273 sensing module a white LED (light-emitting diode) illuminates a probe containing the 274 olive-oil sample and the transmitted light is collected by a digital colour sensor. The 275 microcontroller (MCU) governs the functioning of the system, controlling the 276 measuring module and including the signal-processing algorithms and the standards of 277 the MUOCS and BTB scales. The MCU selected was the PIC18F2550 (Microchip 278 Technology Inc., USA) due to the integration of a USB module in the same chip that 279 allows easy communication with the computer for design and calibration purposes. This 280 device includes five I/O ports that permit the control of the rest of modules of our 281 instrument. The user interface of the portable instrument consists of two buttons that 282 allow the user to select different options through a menu which is presented on the LCD 283 screen. The results of the measurements are also visible on this screen. Furthermore, a 284 software application was developed using Visual Basic 2008 (Microsoft Corp., 285 Redmond, WA, USA). This application uses the MCU USB module to communicate 286 with the instrument and allows the measurement of an olive-oil sample and the 287 modification of the calibration parameters stored on the memory device.



289 Figure 4. Block diagram of the instrument developed.

290

291 **3**.2.1 Sensing module

This module is compounded by a white LED (NSPW300, Nichia, Japan) working as a light source and a S9706 digital colour detector (Hamamatsu Photonics, Japan).

294 The LED source has a typical luminous intensity of 4000 mcd with CIE 1931 colour 295 coordinates of $x=0.33 \pm 0.02$ and $y=0.32 \pm 0.02$ close to those corresponding to the CIE 296 D65 illuminant (x=0.313; y=0.329). For negligible time drift of the LED (Palma et al., 297 2008; León et al, 2006) it is biased by a constant current source that consists of an 298 operational amplifier (the OPA357, Texas Instruments Inc., USA) and micro-power 299 voltage reference (the LM385 of Texas Instruments Inc., USA). This operational 300 amplifier can be switched off by a control signal activated by the microcontroller for 301 reducing the power consumption.

302 The transmitted light through the oil sample is measured by a colour detector, model 303 S9706 (Hamamatsu Photonics, Japan). This device is a digital colour sensor sensitive to 304 red, green, and blue spectral regions, which simultaneously measures the RGB colour 305 coordinates of the incident light. The chip integrates a set of photodiodes for which the maximum sensitivity wavelengths correspond to $\lambda_r = 615$ nm, $\lambda_g = 540$ nm and $\lambda_b = 465$ 306 307 nm. The photocurrent of these photodiodes is on-chip processed to generate a digital output. The signal detected is serially output as 36-bit words, which can be read by the 308 309 MCU without additional signal processing. To enable measurement over a wide range 310 of illuminants, the S9706 detector has two configuration parameters to select its active 311 area and integration time. Internally, the active area of each detector (with dimensions 312 of 1.2×1.2 mm) consists of a matrix of 9×9 silicon photodiodes, with alternating responses in the red, blue, and green colour regions, and can be configured in a highsensitivity mode, where the full area collects the incident light, or in a low-sensitivity mode, where a 3×3 centre area is chosen to be active. In the present work, the highsensitivity mode was chosen in all cases.

In addition to the sensitivity modes related to the selected active area, these colour 317 sensors can externally configure the integration time, i.e. the time interval during the 318 319 photodiode matrix generates a photocurrent for each optical radiation acquisition. This 320 integration time can be easily changed from 10 µs to 100 s with a unique input pin. 321 According to the device datasheet, under constant illumination conditions, the sensor 322 output increases linearly with this time until reaching output saturation. A short 323 integration time means fast acquisition, but with low-intensity light collection, i.e. low 324 sensitivity. Nevertheless, if the integration time is too long, the sensor output could be 325 saturated and therefore a compromise in the integration time value is needed. The 326 response of this sensor was tested as a function of the integration time under the 327 illumination conditions in this application. We found that the shortest time with optimal 328 sensitivity and response time was 2.55 ms and the response output of the digital detector 329 in no case exceeded 85% of its maximum value (López-Álvarez et al, 2009). Finally, 330 the time stability of the S9706 detector response with an integration time of 2.55 ms 331 was checked under continuous illumination. An output-signal drifting lower than 0.1% 332 was found to acquire a signal every 0.2 s for 90 min.

333 The virgin-olive-oil sample under study was contained in a quartz cell of 5-mm 334 pathlength. This specific pathlength has been recommended for virgin-olive-oil colour 335 measurements (Gómez-Robledo et al., 2008), and was the one employed to design the MUOCS standards. The colour detector and the light source were both opposite 336 337 soldered on auxiliary printed circuit boards (PCB) that are fitted to both sides of an 338 opaque structure inside the prototype, as shown in Figure 5. This housing was designed 339 to contain the quartz cell, providing shielding of external light and at the top has a small 340 drawer that can be inserted into the mainframe of the instrument. When the drawer is out, the cell containing the oil sample can be put into the instrument, and then the 341 342 drawer is closed, providing complete optical isolation (see Fig. 5). The real dimensions 343 of the prototype are 15 cm long x 8 cm wide x 5 cm height.



Figure 5. Photography of the instrument showing the panel control, the LCD display
and the sample housing. The dimensions of the prototype are 15 cm long x 8 cm wide x
5 cm high.

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350 **3**.2.2 Power and processing electronics

There are two different operation modes for the instrument: portable mode and 351 computer mode. The instrument can be supplied by the USB port when it is connected 352 353 to a computer, or by two AAA batteries when it works in portable mode. When the 354 device is powered on, and the USB module is disconnected, a DC/DC converter stage 355 raises the 3 V from the batteries to 5 V necessary for the proper functioning of the 356 device. Furthermore, two different 5-V sources are used: one for supplying analogic circuits (red box as shown in Fig. 4), and the second one for digital modules (blue box 357 as shown in Fig. 4). The separation of the power supplies prevents the degradation of 358 359 the measurement due to the electric interference caused by the commutations in digital 360 circuits. If the USB module is connected, the battery is disconnected to save energy and the two 5-V power supplies are obtained from the 5 V provided by the USB module. 361 The device needs to store the whole set of 60 MUOCS and 60 BTB standards, each 362 363 characterized by 3 coordinates. Furthermore, each coordinate has to be stored as a float 364 number to ensure the best classification precision. As the internal EEPROM memory included in the microcontroller had insufficient capacity for this purpose, an external 365 366 EEPROM memory was added to the prototype. The EEPROM memory chosen was 367 25LC1024 (Microchip Technology Inc., USA) which is a 1024 Kbit serial 368 reprogrammable flash memory. The memory is accessed via a simple serial peripheral 369 interface (SPI) compatible serial bus controlled by the MCU.

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- 371 3.2.3 Instrument operation
- 372 The instrument function can be detailed as follows:

373 1. RGB acquisition of the transmitted light (three replicas and averaging) by positioning 374 the quartz cell containing the appropriate sample in the measurement housing. In this step, we must distinguish 3 different measurements made in the following order: 1a) 375 RGB coordinates with the LED source switched off (called RGB_{black}) to take into 376 377 account the potential electronic noise in the measurement. 1b) RGB coordinates for an 378 n-hexane solution placed in the quartz cell (called RGB_{white}). The n-hexane has a refractive index similar to the one of virgin olive oils, and it has been frequently 379 380 employed as reference white in olive-oil colour measurements (Moyano et al., 2008) 381 because it helps compensate for potential secondary reflections of light in the walls of 382 the quartz cell. 1c) RGB coordinates of the olive-oil sample under consideration (called $RGB_{acquired}$). Measurements 1a) and 1b) are made only once at the beginning of a 383 384 session of measurements of different virgin olive oils.

385 2. Signal normalization. The averaged RGB coordinates of the oil sample (RGB_{acquired})
386 were normalized to the white (RGB_{white}) and black (RGB_{black}) reference colours:

$$RGB_{normalized} = \frac{RGB_{acquired} - RGB_{black}}{RGB_{white}},$$

388 3. Transformation of $RGB_{normalized}$ to XYZ tristimulus values, assuming the D65 389 illuminant and CIE 1964 standard colorimetric observer, by a transformation matrix 390 established in the calibration procedure described below (Section 2.2.4). These XYZ 391 tristimulus values were transformed to CIELAB and then to DIN99d coordinates, using 392 the Equations given in Appendix A.

393

4. Computing Euclidean distances in DIN99d colour space, the closest MUOCS and
BTB standards to the virgin-olive-oil sample analysed are found. Once the signal is
processed, the results of the classification (i.e. the closest standards in MUCOS and
BTB scale) are shown on the LCD screen of the instrument, with a total instrument
operation time of 210 ms.

399 If the device is connected to the computer through the USB port, a Visual Basic 400 application takes over control of the instrument. This application was designed to access 401 the calibration parameters stored in the device, i.e. the transformation matrices and 402 equations for translation between different colour spaces (RGB to XYZ and XYZ to 403 CIELAB or DIN99d), RGB values associated with the white and black reference 404 colours and the BTB and MUOCS standards. In this way, a recalibration process could 405 easily be performed.

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407 **3**.2.4. Calibration of the electronic device

408 Calibration of the electronic device designed requires the use of a set of real solutions 409 covering the colour gamut of virgin olive oils. For this, we prepared 10-ml solutions of 410 each of the BTB standards (Figure 6), which were conserved in darkness at ambient 411 temperature for 3 months (Melgosa et al., 2001) before their spectral transmittances 412 were measured (380–770 nm, $\Delta\lambda$ =2 nm) with a JASCO-V650 spectrophotometer (Jasco 413 Europe S.R.L., Cremella, Italy) using quartz cells of 5-mm pathlength. Although the 60 414 BTB standards do not completely cover the real colour gamut of virgin olive oils 415 (Melgosa et al., 2000), we used just these standards instead of an arbitrary set of virgin-416 olive-oil samples with a better gamut, seeking a reproducible calibration method. The 417 results could probably be improved with our instrument by using a calibration set with a 418 larger number of samples than just the 60 BTB standards.

419



- 421 Figure 6. Set of 60 BTB standards prepared for the calibration of our electronic device.
- 422 They are designated (Gutiérrez & Gutiérrez, 1986) as 2/1 (lower left corner) to 2/10 for
- 423 the standards shown in the first column, 3/1 to 3/10 for the second column, etc.

424 Each of our BTB samples was measured 3 times with the JASCO-V650 425 spectrophotometer, and next our portable electronic device measured their 426 corresponding *RGB* values, also 3 times. The repeatability of the 3 measurements 427 performed with our electronic device was good: ± 1 bit (0.025%) in each one of the channels of our RGB 36-bit colour sensor. Spectrophotometric measurements were used 428 429 to compute XYZ tristimulus values, assuming the D65 illuminant and CIE 1964 Supplementary Standard Observer. Then the pseudo-inverse method (Moore, 1920; 430 431 Penrose, 1955) was used to formulate transformation equations from RGB to XYZ. For 432 each of the tristimulus values, second-order equations with 10 coefficients (R, G, B, RG, RB, GB, R², G², B², constant) achieved linear correlation coefficients greater than 433 434 0.989, which were considered acceptable in our case, because they can be implemented 435 in the software of our device. From these equations, our electronic device can measure 436 the XYZ tristimulus values of a virgin-olive-oil sample, and we can convert these values 437 to CIELAB and DIN99d coordinates in order to look for the closest MUOCS and BTB 438 standards to the sample. MATLAB2007b (The Mathworks, Inc., Natick, MA, USA) 439 was used to process the data with a set of scripts and functions developed by us.

440

441 **3.2.5** Performance results

442 A reduced set of 37 commercial virgin olive oils was used to check the accuracy of our 443 electronic device. These commercial oils were randomly chosen trying to cover a wide 444 colour gamut. Samples of each of these oils were measured both with the JASCO-V650 445 spectrophotometer and with our electronic device. On the average, for these commercial 446 oils the colour difference between the two instruments was 3.6 DIN99d units with a 447 standard deviation of 1.5 DIN99d units. These colour differences are not small 448 (Melgosa et al., 1992; Melgosa et al., 2008), but it should be borne in mind that our 449 inexpensive device was not designed to compete with a modern spectrophotometer or 450 colorimeter, but rather simply to provide the MUOCS and BTB standards closest to a 451 given oil sample. In this sense, we should add that for only 3 (i.e. 8%) of our 37 virgin-452 olive-oil samples did the MUOCS classification using our electronic device differ from 453 computations made using the spectrophotometric measurement. This result is very 454 satisfactory and clearly promising, taking into account that the calibration of our 455 electronic device was based on the BTB standards, which fail to cover the whole colour 456 gamut of real virgin-olive-oil samples, and also that some minor modifications were introduced into the electronics of our device between the calibration and the 457 458 measurements of these 37 oil samples.

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462 Appendix A.

464 The equations defining the DIN99d colour space (Cui et al., 2002) from CIELAB 465 coordinates (CIE, 2004) are provided here. First, the CIE tristimulus value X is 466 transformed as follows: X' = 1.12X - 0.12Z

This transformation also applies to the reference white included in conventional CIELAB equations. Next, from CIELAB coordinates L*,a*,b* the following magnitudes are computed:

 $e = a^* cos(50^\circ) + b^* sin(50^\circ)$

 $f = 1.14[-a^*sin(50^\circ) + b^*cos(50^\circ)]$

 $L_{99d} = 325.22 \ln(1 + 0.0036L^*)$

 $G = \sqrt{e^2 + f^2}$

 $C_{99d} = 22.5 \ln(1 + 0.06G)$

 $h_{99d} = \arctan(f/e) + 50^{\circ}$

 $b_{99d} = C_{99d} \sin(h_{99d})$

 $a_{99d} = C_{99d} \cos(h_{99d})$

The final DIN99d colour space is defined by the L99d, a99d, b99d coordinates, and the colour difference between two samples in this space is given by the Euclidean distance:

$$\Delta E_{99d} = \sqrt{\Delta L_{99d}^2 + \Delta a_{99d}^2 + \Delta b_{99d}^2}$$

Appendix B.

Codes and DIN99d coordinates (Cui et al., 2002) of the 60 MUOCS standards are as follows:

| Code | L99d | <i>a</i> _{99d} | b 99d | Code | L99d | <i>a</i> 999d | b 99d |
|---------|-------|-------------------------|--------------|----------|-------|---------------|--------------|
| 1-2-12 | 78.39 | 6.14 | 41.21 | 10-4-8 | 91.89 | 5.27 | 31.41 |
| 2-4-14 | 79.89 | 5.27 | 46.11 | 10-4-11 | 91.89 | 5.27 | 38.76 |
| 3-2-12 | 81.39 | 6.14 | 41.21 | 10-8-6 | 91.89 | 3.54 | 26.51 |
| 3-6-13 | 81.39 | 4.41 | 43.66 | 10-8-9 | 91.89 | 3.54 | 33.86 |
| 4-4-14 | 82.89 | 5.27 | 46.11 | 10-8-12 | 91.89 | 3.54 | 41.21 |
| 5-2-12 | 84.39 | 6.14 | 41.21 | 10-12-4 | 91.89 | 1.81 | 21.61 |
| 5-6-10 | 84.39 | 4.41 | 36.31 | 10-12-7 | 91.89 | 1.81 | 28.96 |
| 5-6-13 | 84.39 | 4.41 | 43.66 | 10-12-10 | 91.89 | 1.81 | 36.31 |
| 5-10-14 | 84.39 | 2.67 | 46.11 | 10-16-11 | 91.89 | 0.08 | 38.76 |

| 6-4-11 | 85.89 | 5.27 | 38.76 | 11-6-7 | 93.39 | 4.41 | 28.96 |
|---------|-------|------|-------|----------|-------|------|-------|
| 6-4-14 | 85.89 | 5.27 | 46.11 | 11-6-10 | 93.39 | 4.41 | 36.31 |
| 6-8-9 | 85.89 | 3.54 | 33.86 | 11-10-5 | 93.39 | 2.67 | 24.06 |
| 6-8-12 | 85.89 | 3.54 | 41.21 | 11-10-8 | 93.39 | 2.67 | 31.41 |
| 6-12-13 | 85.89 | 1.81 | 43.66 | 11-10-11 | 93.39 | 2.67 | 38.76 |
| 7-2-12 | 87.39 | 6.14 | 41.21 | 11-14-9 | 93.39 | 0.94 | 33.86 |
| 7-6-7 | 87.39 | 4.41 | 28.96 | 12-8-3 | 94.89 | 3.54 | 19.16 |
| 7-6-10 | 87.39 | 4.41 | 36.31 | 12-8-6 | 94.89 | 3.54 | 26.51 |
| 7-6-13 | 87.39 | 4.41 | 43.66 | 12-8-9 | 94.89 | 3.54 | 33.86 |
| 7-10-14 | 87.39 | 2.67 | 46.11 | 12-12-1 | 94.89 | 1.81 | 14.26 |
| 8-4-11 | 88.89 | 5.27 | 38.76 | 12-12-4 | 94.89 | 1.81 | 21.61 |
| 8-4-14 | 88.89 | 5.27 | 46.11 | 12-12-7 | 94.89 | 1.81 | 28.96 |
| 8-8-6 | 88.89 | 3.54 | 26.51 | 13-10-2 | 96.39 | 2.67 | 16.71 |
| 8-8-9 | 88.89 | 3.54 | 33.86 | 13-10-5 | 96.39 | 2.67 | 24.06 |
| 8-8-12 | 88.89 | 3.54 | 41.21 | 13-10-8 | 96.39 | 2.67 | 31.41 |
| 8-12-13 | 88.89 | 1.81 | 43.66 | 13-14-3 | 96.39 | 0.94 | 19.16 |
| 9-2-12 | 90.39 | 6.14 | 41.21 | 14-8-3 | 97.89 | 3.54 | 19.16 |
| 9-6-7 | 90.39 | 4.41 | 28.96 | 14-12-4 | 97.89 | 1.81 | 21.61 |
| 9-6-10 | 90.39 | 4.41 | 36.31 | | | | |
| 9-6-13 | 90.39 | 4.41 | 43.66 | | | | |
| 9-10-5 | 90.39 | 2.67 | 24.06 | | | | |
| 9-10-8 | 90.39 | 2.67 | 31.41 | | | | |
| 9-10-11 | 90.39 | 2.67 | 38.76 | | | | |
| 9-14-12 | 90.39 | 0.94 | 41.21 | | | | |

503

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a.,,,

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Figure 4

Figure 5

| Lightness | L _{99d} | Green Hue | a _{99d} | Yellow Hue | b 99d |
|-----------|------------------|-----------|-------------------------|------------|--------------|
| 1 | 78.39 | 2 | 6.14 | 1 | 14.26 |
| 2 | 79.89 | 4 | 5.27 | 2 | 16.71 |
| 3 | 81.39 | 6 | 4.41 | 3 | 19.16 |
| 5 | 84.39 | 8 | 3.54 | 4 | 21.61 |
| 4 | 82.89 | 10 | 2.67 | 5 | 24.06 |
| 6 | 85.89 | 12 | 1.81 | 6 | 26.51 |
| 7 | 87.39 | 14 | 0.94 | 7 | 28.96 |
| 8 | 88.89 | 16 | 0.08 | 8 | 31.41 |
| 9 | 90.39 | - | - | 9 | 33.86 |
| 10 | 91.89 | - | - | 10 | 36.31 |
| 11 | 93.39 | - | - | 11 | 38.76 |
| 12 | 94.89 | - | - | 12 | 41.21 |
| 13 | 96.39 | - | - | 13 | 43.66 |
| 14 | 97.89 | - | - | 14 | 46.11 |