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ORIGINAL PAPER

Multifunction spectrometer for optical inspection of red wine

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Abstract The main goal of this study was to develop an apparatus that makes it possible to measure both, color, refractive index and light scattering (turbidity) of red wines using a single device only. Typically such measurement of red wine quality requires three different measurement devices. As an example of the efficiency of the present device we studied the change of the thermo-optical and time-dependent optical properties of red wine samples. Here we report on change of optical properties of two Merlot wine samples, which were obtained by opening authentic red wine bottles and preserving a set of samples both at room and refrigerator temperature for 26 days, respectively. The interesting feature with both red wine samples was that the light scattering, i.e. the turbidity of the samples, increased as a function of time due to oxidation process. It is suggested that the multifunction spectrophotometer can be applied for optical inspection of red and other wine products.

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Introduction

Red wine is a rather complex fluid. It contains water, alcohol, acids, phenolic compounds, sugar, and other compounds [1]. Measurement of only one quality parameter of red wine doesn't give the inspector enough information of the whole red wine—one needs usually a general view of the red wine quality i.e. several measurements and observations. Optical spectroscopy is one of a number of techniques that can be applied to the inspection of the red wine quality. Then the refractive index, transmittance, and turbidity of the red wine can provide information about alcohol per cent, color and clarity of wine, respectively. In general, the advantage of optical measurement techniques lies in their rapidity, simplicity, relatively low running costs, and versatility.

Color is one of the main parameters of the quality of wines, especially red wine. The color provides information about defects, and the type and the conservation of wines during storage [2]. Red wine color measurements are based on the absorbance of monomeric anthocyanin pigments and polymeric pigment forms in the visible spectral region. Additional spectral information about red wine can be obtained by recording transmission spectrum also at the ultra-violet spectral range. Transmission measurements are typically performed using a cuvette, with path length between 1 and 2 mm, for the detection of the light transmission. For color analysis of red wines a specific color density and hue are commonly used. The color density is defined as the combined absorption $A_{420} + A_{520} + A_{620}$ at three wavelengths 420, 520 and 620 nm, while the hue is a

ratio A_{420}/A_{520}. The hue is related to the "chemical aging" of the wine. As the wine ages and matures, a characteristic hue shifts from 0.4–0.5 to 0.8–0.9 [3].

Refractive index measurement is an important quality control procedure commonly used in the food industry that allows one to determine whether a sample is in pure form or to quantify the amount of solute in a solution. In the wine making process, refractive index measurements are routinely used to determine sugar content of grapes (optimum time harvested) and alcohol content of the finished wine. The refractive index of wine and liquids is typically determined by measuring the critical angle of reflection of incident light at the wavelength 589.3 nm (D1-line of sodium) by using a commercial Abbe refractometer. Unfortunately, Abbe refractometer provides only limited information, and the refractive index reading is highly disputable in the case that the liquid absorbs light at 589.3 nm. Therefore, we have put efforts to design and build an apparatus that gives more reliable and more comprehensive data on optical properties of different kind of liquids. This resulted to the construction of the multi function spectrophotometer (MFS). MFS is a multi function device that provides information on various optical properties of liquids at relatively wide UV–visible spectral range [4–6] instead of the typical single wavelength of the D1 line of sodium.

Turbidity is the name given to one of the optical properties of a liquid in the presence of concentration of materials whether solids, emulsions or immiscible fluids that differ from the host liquid [7]. Turbidity is by convention measured using a single wavelength or white light and detectors at 0° and 90° angles with respect to the incident light beam. These instruments are known as turbidimeters or nephelometers and are calibrated in units of NTU. In the wine industry, turbidimeters are used for monitoring of filtration process of wine and determine deposition of the finished wine. Commercial turbidimeters give only one reading, whereas the MFS provides a scattering spectrum. Hence, the data of the MFS can be considered more comprehensive than that of a conventional device for turbidity detection.

The future trend of red wine and other drinks quality monitoring by optical techniques will rely on multi function measurements. Recently, a multi-parameter fiber-optical sensor was developed for the simultaneous monitoring of color and the refractive index of the red wine [8]. A portable spectronephelometer for port wine has been developed for in situ monitoring of the success of the filtration process by measuring the color and turbidity of the wine [9]. We recently proposed a method for the authenticity of red wine, which was based on color, refractive index and turbidity measurements [10]. That study used three different devices, whereas here we have coupled the three measurement modes into one apparatus namely the MFS. To test the MFS in red wine inspection we measured data from opened red wine bottles that were preserved both at room temperature and in a refrigerator.

Materials and methods

Samples

Optical properties of authentic red wines from Chile and France were investigated. Both wines were 100% Merlot grape. The alcohol percentage of Chilean wine was 14.0 vol.%, dry extract 31 g/l, sugar <1 g/l and total acids 5.1 g/l. The corresponding values of the French wine were 12.5 vol.%, 30 g/l, 4 g/l and 5.3 g/l, respectively. The red wine bottles were bought from Alko Inc., which is alcoholic beverages retail sales monopoly in Finland. The red wine samples were divided into two laboratory bottle sets. One bottle pair was preserved at the room temperature (21°C) and cork closed in a dark box. The other pair was preserved in a refrigerator at 5°C in dark and also cork closed, but before measurement it was stabilized to the temperature 21°C. There sample bottles were full of red wine but there was a little amount of air inside. During the course of measurements a small portion of red wine sample was lost because of pumping it into the measurement cavity of the MFS.

Multifunction spectrophotometer (MFS)

We measured the transmission, the reflection and the scattering using the MFS shown in Fig. 1. The light source included a 150 W xenon lamp and a monochromator. Emitted light is guided into a bifurcated optical fiber. The usable spectral range of the present device is 270–800 nm. The output end of the fiber can be considered as a point source and when it is set at the focal point of a parabolic reflector, a collimated light beam is generated. The collimated light beam is directed to a chopper. The innovation of the MFS is to use a Dove prism instead of a conventional equilateral or right angle prism. The geometry of the Dove prism makes it possible to measure light transmission in addition to the light reflection and scattering. Linearly polarized light beam propagates towards the prism and the sample interface. The angle of incidence can be varied with a step motor-driven rotator. The minimum increment of movement of the step motor corresponds to a rotation angle of 0.005°. However, typically a step equal to 0.1° is adequate for most of the cases.

The system is based on a well-known two-detector scheme (numbers 1 and 2 in Fig. 1), i.e., simultaneous detection of the signal and the reference ratio. In the case of Fig. 1a the detector 1 was used for the measurement of

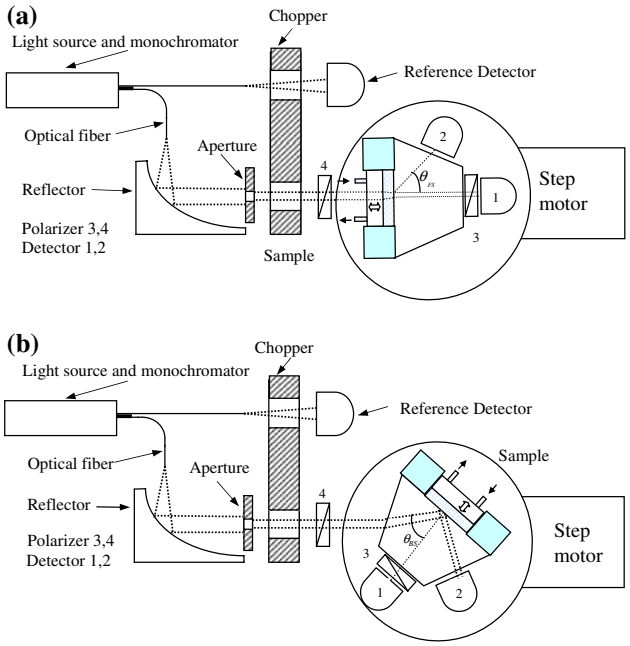

Fig. 1 Schematic diagram of the multifunction spectrophotometer

transmittance, but in Fig. 1b it was used for the detection of light scattering in the forward direction. Detector 2 in turn was used for the measurement of the reflectance (see Fig. 1b), or for forward light scattering (see Fig. 1a). In the transmission measurement mode a removable polarizer (number 3 in Fig. 1) can be used in order to detect the rotation of the polarization of light of optically active liquids, as shown in Fig. 1a. Polarizes 3 & 4 are crossed in the detection of optical activity in case of samples containing sugar.

The liquid sample was circulated between the container and the sample compartment using a peristaltic pump. The sample compartment consisted of a free space between the prism face and a window. Depending on the optical density of liquids the optical path length in the transmission measurement mode can be adjusted between 2 and 15 mm by moving the window. The window positioning is managed using a micrometer screw. A more detailed technical description of the MFS can be found in Ref. [11].

Measurements were carried out for 26 days, i.e., reflection data as a function angle of light incidence, and transmission, scattering and reflection as a function of wavelength.

Results

Color analysis

The transmission spectra (380–750 nm) were measured at 1.0 nm intervals with sample path length 2.5 mm. The transmittance can be calculated using the Beer-Lambert law

$$T(\lambda) = \frac{I^{\text{wine}}(\lambda)}{I^{\text{water}}(\lambda)} = \exp(-l\alpha), \quad (1)$$

where λ is the wavelength of light, α the absorption coefficient of the sample and l is the length that the light travels through the wine. Due to the oxidation in an opened red wine bottle the transmittance typically decreases as a function of time as shown in Fig. 2 for the wine from Chile and France. The transmittance difference was rather small between the samples preserved at the room temperature and the refrigerator. Nevertheless, temporal changes are considerable as shown in Fig. 2. The transmission data can be utilized in color inspection of red wine.

The red wine color analysis is based on the CIE 1976 $L^*a^*b^*$ (CIELAB) color space. Color is defined by parameters L^* = lightness (or clarity) of the color ($L^* = 0$ yields black and $L^* = 100$ indicates white), a^* = position between red and green (green indicates negative values and red positive), and b^* = position between yellow and blue (blue indicates negative values and yellow positive). In current red wine color analysis value a^* was positive (indicating changes in red) and value b^* was also positive (indicating changes in yellow). The color difference ΔE^*_{ab} between two color stimuli is calculated as the Euclidean distance between the points in the CIELAB color space [12]. In theory the ΔE value 0.5 is enough for human eye to perceive [13]. However, daylight human vision (also known as, photopic vision) is most sensitive to the green region of the color spectrum around 550 nm, and least sensitive to colors near the extremes of the visible spectrum (deep blue-purples at one end and deep reds at the other). For that reason, color differences in the latter regions (e.g. the red wine color differences) are harder for the average human observer to detect and quantify, making ΔE measurements for those colors possibly less accurate [12]. Thus, in case of red wine, the ΔE values between 0.5 to 1 in color difference evaluation are more suitable to be used as the minimum ΔE for human eye to perceive. All the data used in color analysis was calculated from the Chilean and French red wine transmittance data recorded during 26 consecutive days.

Red wine color estimation in alcohol laboratories is often based on the CIELAB color space under the standard D65 illumination (average daylight) [14]. Visual color estimation is performed under indoor light sources, e.g. incandescent lamps or fluorescent tubes or their mixture. Based on this we chose to simulate our red wine color under light sources D65 (daylight), A (incandescent light) and F2 (fluorescent tube, "office light").

The CIELAB color analysis enables us to perform more detailed color analysis than would be possible by only

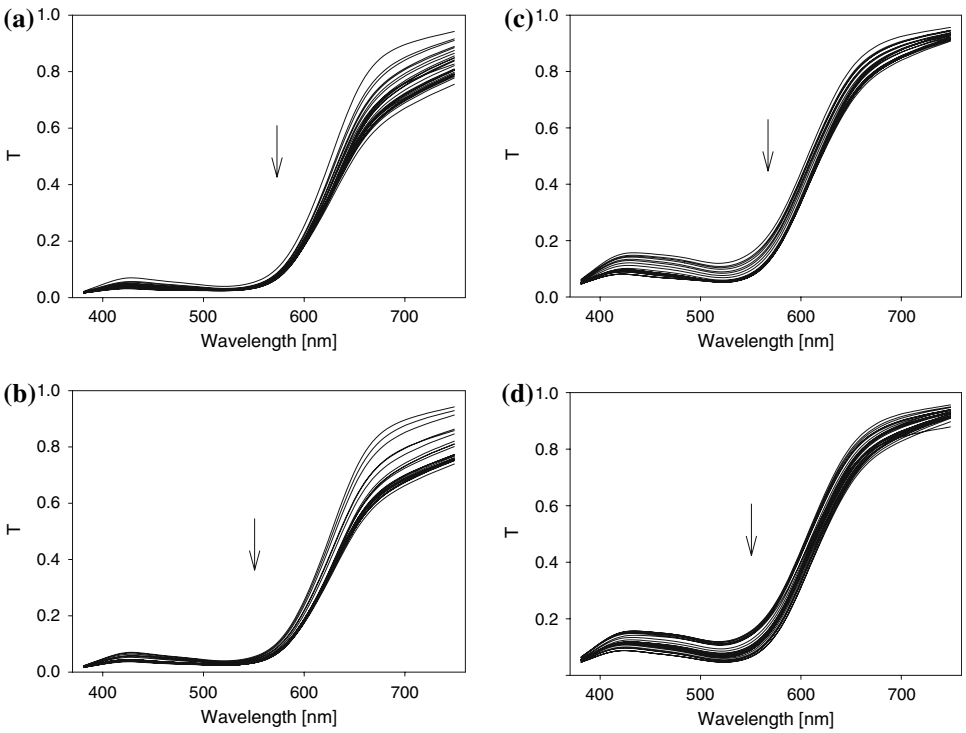

Fig. 2 Red wine from Chile (**a**) storage in dark and at room temperature, and (**b**) in dark and in refrigerator**,** red wine from France (**c**) storage in dark and at room temperature, and (**d**) in dark and in refrigerator. The arrow indicates the direction of change of transmission as the time is increasing

evaluating the "raw" transmission spectra. The oxidation in wine can be observed from Figs. 3a and 4a as well, as the L^* parameter gradually becomes smaller, thus red wine color becomes darker. In Chilean red wine room data (Fig. 3a) we can observe that the L^* does not become any darker after day #9, instead a^* becomes less red even quicker than before. In the Chilean red wine refrigerator color data, similar changes as in room data occur after day #8. In addition, when we reach the last day #26, color of the red wine is less red in the refrigerator sample than in the room sample. Figure 3b shows us that the Chilean red wine b^* value becomes yellower. This effect is less dramatic in refrigerator samples. Thus, storage temperature changes obviously affect the changes in red wine visual color.

In Fig. 4a French red wine color changes can be observed. Also in this case the oxidation phenomenon can be seen. The difference to Fig. 3a is that a^* (red value) becomes higher. We can also detect that L^* does not become significantly darker after day #10 (room) and day #24 (refrigerator), but slightly less red. In addition, the day #4 refrigerator data shows a small "color anomaly". Figure 4b room data shows darkening associated to color changes after day #10 (room) and day #24 (refrigerator), b^* becomes yellower (especially in "room") vs. a^* becomes slightly less red. Naturally, in all figures the scale of red wine $L^*a^*b^*$ value changes depend on light sources used for evaluation.

Figure 5 shows color difference ΔE between Chilean red wine refrigerator sample and room sample, 26 consecutive days and Fig. 6 shows color difference ΔE between French red wine refrigerator sample and room sample, 26 consecutive days both simulated under 3 different light sources. All color differences in Fig. 5 can be detected very well by human eye. In addition, there seems to be an "increasing values trend" in Chilean red wine room vs. refrigerator color difference ΔE towards the 26th day. In case of the French wine in Fig. 6, the color differences between the room vs. the refrigerator data are even more significant. This time the color difference values increase towards 10th day, then they slightly decrease and finally reach their highest values towards the 26th day. The F2 light source (fluorescent tube) gives the highest color differences in both cases.

Figure 7 shows color difference ΔE between Chilean red wine Day 1 room sample and 25 consecutive day's room sample and similarly, Day 1 refrigerator sample and 25 consecutive day's refrigerator sample. Similar color difference data ΔE for French red wine can be seen in Fig. 8. In case of Chilean red wine the color differences to Day 1 can be perceived and in addition, the room data is quite similar to the refrigerator data. However, in Fig. 8 French red wine room data is quite different from refrigerator data until day #22. Compared to data in Fig. 7 the color differences are generally larger. Table 1 shows red wine color difference ΔE between consecutive days. Simulations under three light sources are very similar to each other, thus, only D65 simulation is shown. We can see from the Table 1 that only color differences between

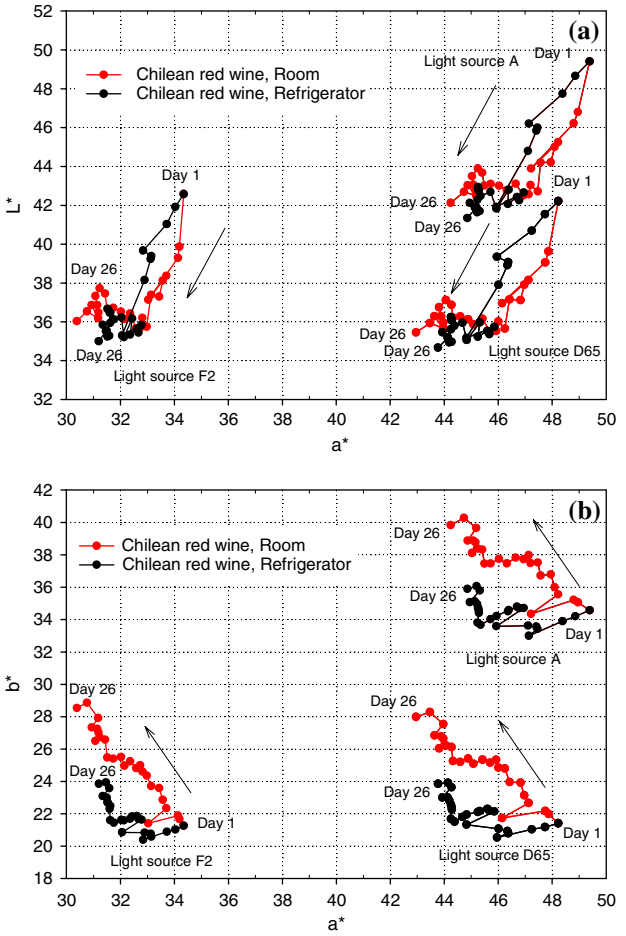

Fig. 3 (**a**) Chilean red wine CIE L^*a^* (**b**) and a^*b^* values. 26 consecutive days simulated under light sources A (incandescent), D65 (average daylight) and F2 (fluorescent tube, "office light")

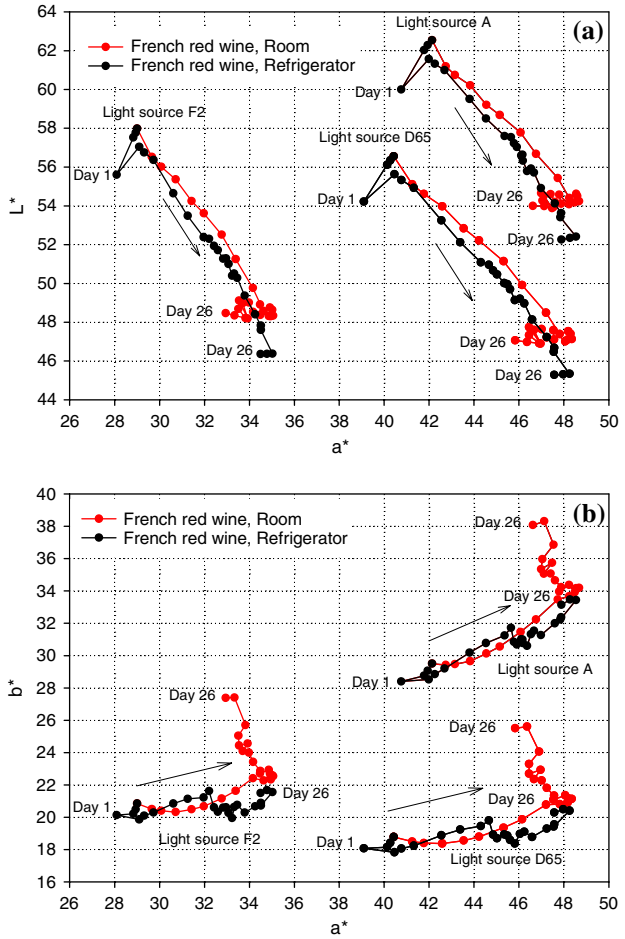

Fig. 4 (**a**) French red wine CIE L^*a^* (**b**) and a^*b^* values. 26 consecutive days simulated under light sources A (incandescent), D65 (average daylight) and F2 (fluorescent tube, "office light")

consecutive days 1–2, 3–4, 4–5, 6–7, and 8–9 can be detected by human eye.

Complex refractive index and turbidity analysis

We measured reflectance from the red wine samples as an angle of function using s-polarized light and fixed wavelength 589.6 nm. The complex refractive index (complex number) of a red wine can be approximated, by fitting the recorded reflectance curve to Fresnel's equation [15] as follows:

$$R_s = r_s r_s^* = \left(\frac{\cos\theta_i - \sqrt{N_{21}^2 - \sin^2\theta_i}}{\cos\theta_i + \sqrt{N_{21}^2 - \sin^2\theta_i}}\right)\left(\frac{\cos\theta_i - \sqrt{N_{21}^2 - \sin^2\theta_i}}{\cos\theta_i + \sqrt{N_{21}^2 - \sin^2\theta_i}}\right)^*, \quad (2)$$

where (*) denotes the complex conjugate, r_s is the complex reflection coefficient , $N_{21} = (n_1 + ik_1)/n_2$ is the relative complex refractive index of the red wine and the prism system, "1" denotes the wine, "2" the prism, and θ_i is the angle of light incidence. The dispersion properties of the prism were a priori known. In the data fitting procedure

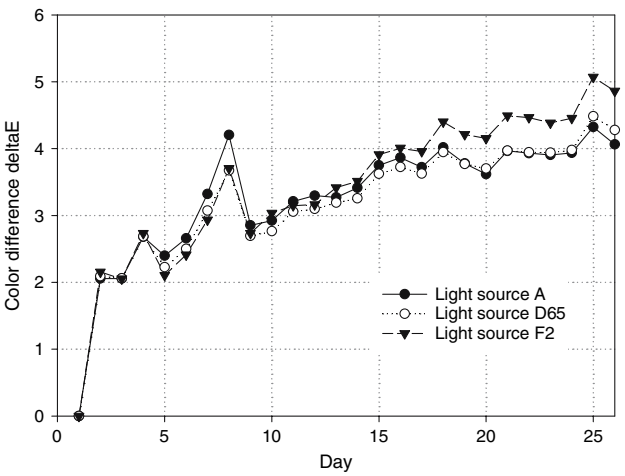

Fig. 5 Color difference ΔE between Chilean red wine refrigerator sample and room sample, 26 consecutive days

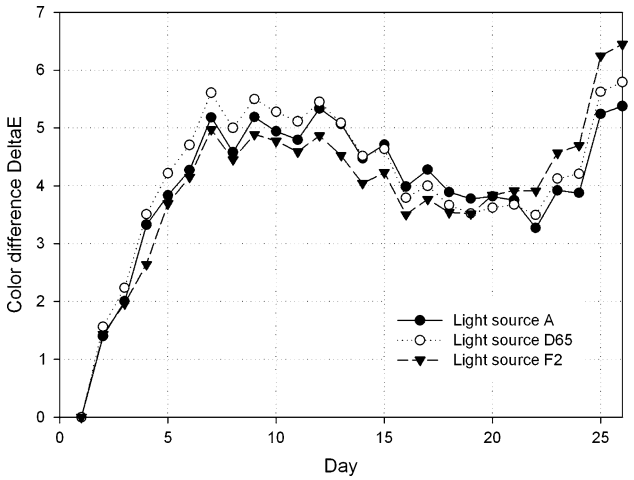

Fig. 6 Color difference ΔE between French red wine refrigerator sample and room sample, 26 consecutive days

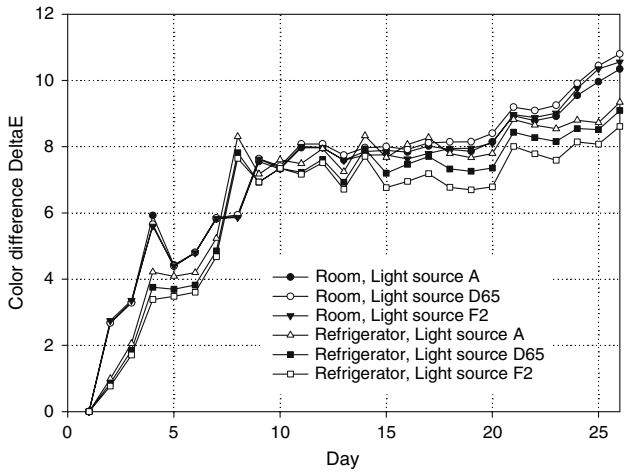

Fig. 7 Color difference ΔE between Chilean red wine Day 1 room sample and 25 consecutive day's room sample and similarly, Day 1 refrigerator sample and 25 consecutive day's refrigerator sample

the real and imaginary parts of the complex refractive index are changed until theoretical and measured reflectance are the same or as close as possible to each other. This is implemented by minimizing the sum

$$S(N_{21}) = \sum_{i=1}^{M} \left(R_{\mathrm{mi}} - R_s(\theta_i, N_{21})\right)^2 \qquad (3)$$

where R_{mi} is the measured reflectance at the angle of incidence θ_i and R_{s} is the theoretical reflectance calculated using Eq. (2). As an example of this procedure, we can see in Fig. 9 the decrease of the refractive index (real part of the complex refractive index) of the red wine as a function of time at the wavelength 589.6 nm. The refractive index of Chilean red wine changed from 1.3460 to 1.3438 and French red wine from 1.3441 to 1.3420**.** The change of the

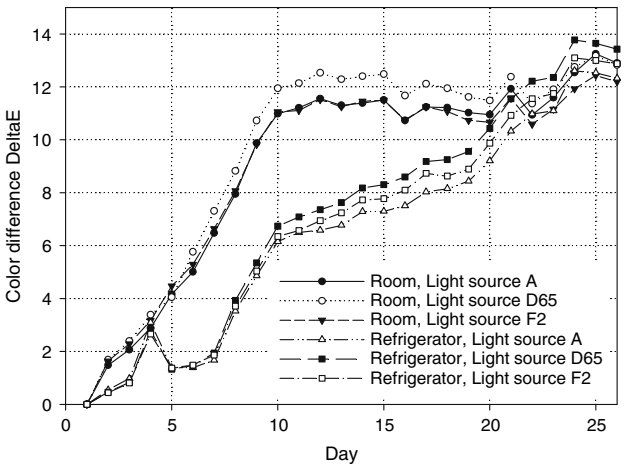

Fig. 8 Color difference ΔE between French red wine Day 1 room sample and 25 consecutive day's room sample and similarly, Day 1 refrigerator sample and 25 consecutive day's refrigerator sample

Table 1 Red wine color difference ΔE (under CIE D65 light source) between consecutive days

Days	Chile Room D65	Chile Fridge D65	France Room D65	France Fridge D65
1–2	2.67	0.86	1.68	0.46
2–3	0.61	0.99	0.73	0.37
3–4	2.67	1.93	1.04	2.16
4–5	1.80	0.56	1.50	1.97
5–6	0.55	0.22	0.95	0.49
6–7	1.13	1.07	1.63	0.71
7–8	0.41	2.99	1.57	2.17
8–9	1.73	1.43	2.00	1.45
9–10	0.44	0.42	1.26	1.40
10–11	0.70	0.22	0.55	0.52
11–12	0.28	0.50	0.43	0.95
12–13	0.72	0.74	0.28	0.35
13–14	0.51	1.05	0.38	0.60
14–15	0.46	0.92	0.47	0.16
15–16	0.37	0.44	0.82	0.40
16–17	0.28	0.28	0.54	0.64
17–18	1.09	0.74	0.59	0.65
18–19	0.34	0.35	0.67	0.33
19–20	0.48	0.21	0.36	0.96
20–21	1.01	1.22	0.96	1.22
21–22	0.37	0.32	1.01	0.70
22–23	0.26	0.33	0.74	0.25
23–24	0.98	0.87	0.98	1.66
24–25	0.93	0.37	1.64	0.30
25–26	0.77	0.62	0.55	0.45

refractive index is relatively small. The change is probably apparent, because due to the turbidity of the red wine scattering of light may present a noise in the reflectance

signal. One reason may also be the evaporation of the alcohol of the sample.

We measured also the reflectance from red wine samples as a function of wavelength, using s-polarized light, and the angle of light incidence was fixed to 66.9°. We can solve the wavelength-dependent real refractive index (n_1) of the red wine from Eq. (2) when the extinction coefficient (k_1) is first calculated using transmission data and a relevant formula given in [16]. The results of such an analysis for Chilean red wine are shown in Fig. 10. Here again the refractive index tends to decrease as a function of time. Naturally, the reason is the increase of the turbidity of the red wine sample.

The scattering of light was measured in the forward θ_{FS} (60°) scattering direction with 8 mm path length and at the wavelength range 380–750 nm. The turbidity was calculated as the ratio for the spectrum of the red wine and purified water as follows [9]:

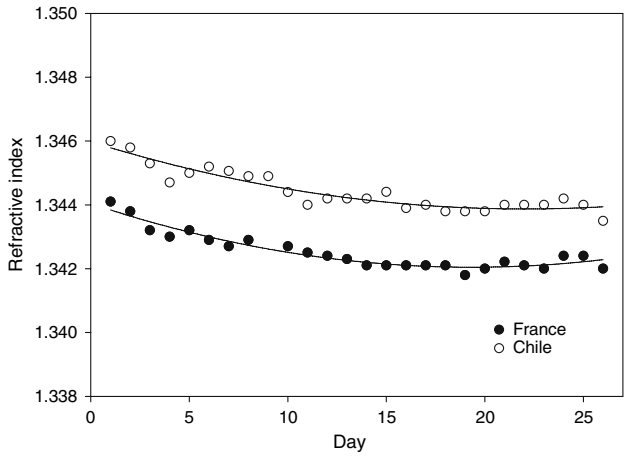

Fig. 9 Refractive index change as a function of time and for room temperature samples

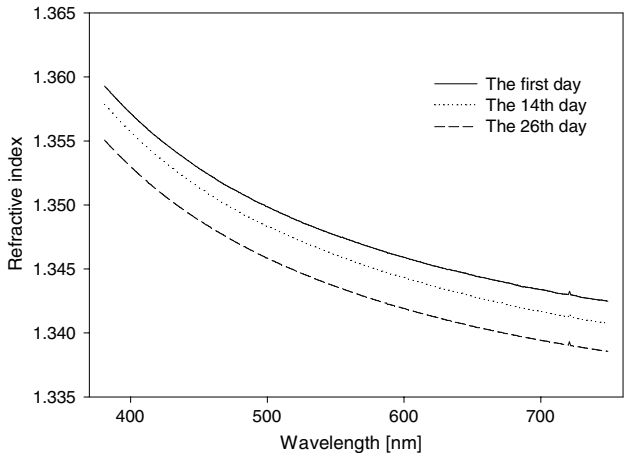

Fig. 10 Refractive index of Chilean red wine as a function of wavelength. The sample is at room temperature

$$\tau(\lambda) = \frac{I^{\text{wine}}(\lambda)}{I^{\text{water}}(\lambda)}. \quad (4)$$

We observe from Fig. 11 that the turbidity of red wine is observed only once the wavelength is over 650 nm. This is consistent with the fact that the red wine absorbs strongly light below 650 nm. Here the scattering signal gets stronger as a function of time. It is an evidence of the creation of light scattering units in the red wine sample (solid materials) due to the oxidation**.** The light scattering of the Chilean red wine increased ten times in magnitude between the first and the last scattering measurement, whereas the turbidity of the French wine increased three times at the wavelength 720 nm. Due to the low light scattering level in Fig. 11b the accuracy of the absolute value of the turbidity is lower than in the case of Fig. 11a. Of course the scattering intensity depends on the thickness of the sample. In highly turbid wines multiple scattering of light will eventually be present. Multiple scattering occurs when the photon's free path for elastic scattering is much

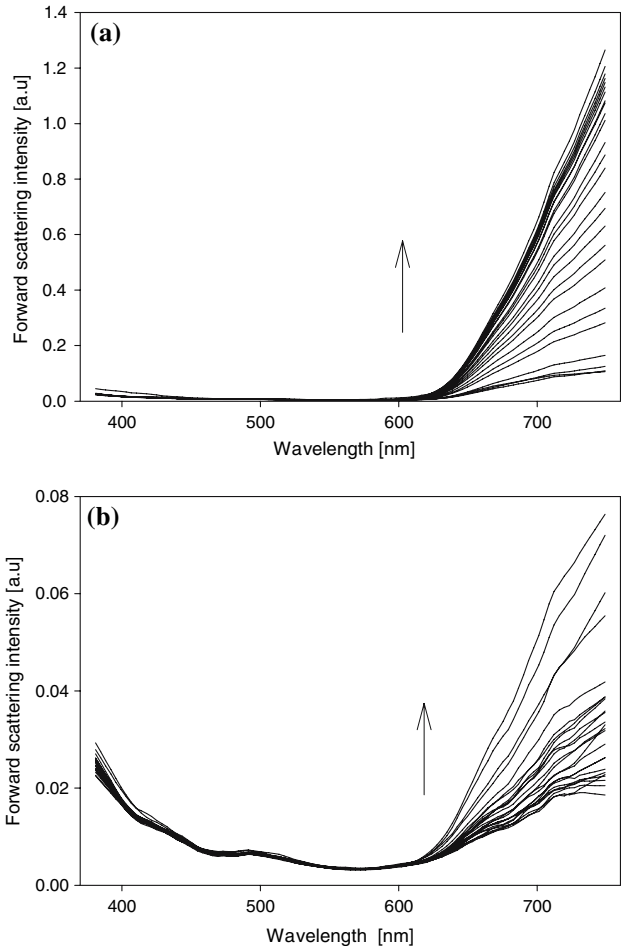

Fig. 11 Forward scattering of light as a function of wavelength (**a**) for Chilean wine and (**b**) French wine. The signal is proportional to turbidity

more smaller than the sample length. In addition, small "CO_2" bubbles may disturb in the turbidity measurement, but this problem can be avoided by pressurization sample compartment.

Conclusions

We have reported construction of a practical multifunction spectrophotometer for the determination of various optical properties of the red wines. The key point is that overall inspection of a wine can be done using only one instrument. From the measured data it is possible to calculate different optical properties of the samples, such as the real refractive index, extinction coefficient, color and turbidity. Hence the time consumption, space requirement, managing of different practises, calibration and also maintenance can be reduced. The current procedure of three measurements by MFS takes 10 min. Another advantage of the MSF over the conventional devices is the possibility to record spectra. Here we demonstrated the utility of the MFS in the inspection of time- and temperature dependent changes of red wines. Naturally, for comprehensive statistical analysis the number of red wine samples should be much higher than two. If sugar content of a sweet wine is an issue the optical activity can be measured by rotation of the polarisers of the MFS.

We suggest that the developed MFS will, on one hand, help wine makers to monitor their wine quality using one device only instead of the conventional three different devices, and on the other hand assist relevant authorities to control the red wine products on the markets. The next step is to build a portable MFS, which can be used for various type on-line and other inspection purposes of red and white wines, beer etc.

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