Spectroscopy and Whisky

Frederik Würtz Sørensen & Thomas Toft Lindkvist

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I. Introduction

Most of the information we receive on a daily basis is in the form of varying electromagnetic fields, e.g. visible light. Naturally, then, the study of the interaction between matter and electromagnetic radiation is of utmost importance - a study known as *spectroscopy*. Here the aforementioned interaction as a function of wavelength or frequency is scrutinized, and this has become an integral exploratory tool in the fields of physics, chemistry and astronomy. In the following we will be looking at spectral lines, and how they can be used to both calibrate a spectrometer, but also identify the molecular makeup of stars and atmospheres. Furthermore, we will be looking at UV-VIS absorption of 15 different whiskies in an attempt to tell them apart.
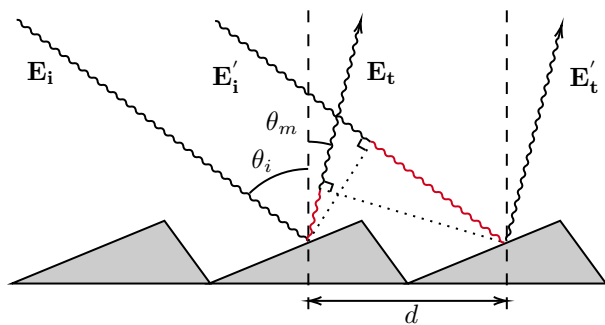
II. Theory

Figure 1: Two representations of parallel monochromatic coherent plane light waves, E_i and E_i', incident on a periodic grating of characteristic spacing d.

A. Analyzing EM radiation

A spectrometer is any scientific device, which separates and measures the spectral components of a physical phenomenon. The grating spectrometer utilizes a periodic, reflective microscopic structure to achieve interference. A schematic view of the situation is seen on figure 1. Here, two representations of parallel monochromatic coherent plane light waves, $\mathbf{E}$ and $\mathbf{E}'$, with wavelength λ impinges on a grate with characteristic spacing d. A

dashed line marks the reflection of , when the two waves are still in phase, per assumption. For the two waves to interfere constructively after the reflection of $\mathbf{E}'$, they need still be in phase. This only happens when the discrepancy in path length travelled by the two waves, illustrated in red on figure 1, differ by a multiple of $m\lambda$ for $m \in \mathbb{Z}$. Simple trigonometry yields the so-called grating equation

$$d\left(\sin\theta_i - \sin\theta_m\right) = m\lambda \tag{1}$$

As seen from eq. 1 longer wavelengths will be diffracted more than shorter resulting in the light being split into it's components, similar to a prism. By choosing an appropriate value d, one can transfer a specific set of diffracted waves (with $m = 1$), onto an array of light sensitive elements, pixels. Since different wavelengths diffract differently, the initial beam will be split physically and hit across the range of this array, with shortest wavelength in one end and longest in the other. This arrays of pixels is called a charge-coupled device (CCD), and works by the photo-electric effect. Photons upon incidence with a pixel will result in a measurable electrical signal.

B. Spectral lines

Upon observing an otherwise smooth and continuous spectrum of light, a spectral line is an abrupt and narrow change in intensity. These occur as either emission lines or absorption lines, and are direct consequences of a quantum system interacting with individual photons. Given a quantum system, e.g. an atom or a molecule, one can identify all the allowed states and their corresponding energies. Upon interaction with light so-called *transition rules* govern the allowed transitions between quantum states. A photon with energy near the discrepant energy between two states of an *allowed* transition, near *resonance*, may be absorbed by the quantum system, which then evolves into the higher energy state. After a while, the system may decay into the lower energy state by isotropic emission of a photon, returning to some lower energy state.

For gaseous elements, this can be exploited in the *gas-discharge* lamp. Such a device enforces a voltage between an anode and a cathode on either end of a gas-filled tube. In operation, neutral atoms (or molecules)

near the anode are stripped of an electron, causing the newly-formed cation to move towards the cathode, due to the electric field [11]. Typically, the cation will swiftly collide with another neutral atom from which it may gain an electron and become neutral again, but now in a higher-energy quantum state, as a result of the extra kinetic energy. For this reason the gas is usually kept at a low pressure to increase the mean free path of the moving ions, thus increasing the mean acquired kinetic energy. Upon returning to a lower-energy quantum state, the atom emits a photon of a characteristic wavelength. The electron donor, newly ionized, undergoes the same process, and thus, as a chain of relaying ions, allowing current to flow - all the while radiating photons at characteristic wavelengths. Quickly, a steady spectrum will emerge and, like a quantum fingerprint, these emission lines may allow one to determine the atomic or molecular composition of the gas.

C. Absorbance

A physical body which absorbs all incident electromagnetic radiation, regardless of frequency or angle of incidence is called a *blackbody*. Such an idealized body will emit light according to Planck's Law, i.e. for an absolute temperature T, the spectral radiance at a frequency ν, is given by

$$B(\nu, T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{\frac{h\nu}{k_B T}} - 1},$$ (2)

where h is Planck's constant.

Suppose light from such a blackbody is impeded by a relatively cold collection of a single element or molecule in gaseous form. Assume that this collection has a vastly different Planck spectrum, such that their intrinsic radiation may be ignored. Now, as described, upon excitation and de-excitation the effect of the isotropically emitted photons will be to reduce the average intensity near resonant frequencies.

A near-perfect blackbody is found in the center of our sun, and as the energy radiates through the outermost part of the gaseous star, this very process occurs. The resultant characteristic spectral lines make it possible to identify the molecular makeup of the solar atmosphere, or, indeed, the atmospheric makeup of most other observable stars. When observing the sun from earth, the spectrum also contains telluric lines, i.e. absorption lines from the atmosphere of the earth, mainly from oxygen.

In general when light is shining through an absorbant material, the reduced intensity is quantified as the absorbance, defined by

$$A = \log \frac{I_{in}}{I_{out}}.$$ (3)

Lambert-Beers law relates the absorbance to a solution through which the light has passed as

$$A = n\sigma l,$$ (4)

where n is the number density, σ is the absorption cross section and l is the path length through the solution.

When looking at absorbance of larger molecules, we do not see sharp dips, as had it been atoms. The larger structure makes vibration possible. This means that in each electronic state multiple vibrational state exist, with the number of possible vibrational modes being equal to the number of degrees of freedom — $3N - 6$ for non-linear molecules, with N being the number of atoms. The electronic and vibrational state combine to give specific vibronic states.

In accordance with the Maxwell-Boltzmann distribution the absolute ground state won't be fully populated, many of the higher vibrational states in the electronic ground state will be too. When exciting the molecule to a higher electronic state, the Franck-Cordon principle states that the most probable vibronic transition, is the one where the nuclei move the least between transition, as the electronic transition is much faster than nuclear motion [9].

In the language of quantum mechanics - the transition probability is proportional to the overlap between nuclear wavefunctions of the two vibronic states.

$$P \propto \langle \nu_1 | \nu_2 \rangle$$ (5)

In general, the distance in energy between two vibrational states in the same electronic state, is quite small compared to the distance between electronic states. This gives rise to many closely spaced vibronic resonances, and widens the absorption spectrum for a specific electronic transition. Upon cooling of the molecules, the absorption spectrum narrows as vibrational modes in the ground state are being frozen out - again in accordance with the Maxwell-Boltzmann distribution. But we will be working at room temperature, so some of these higher states will be populated.

Another effect of temperature is Doppler broadening, which will broaden each of the vibronic transitions considerably. [4, p. 151]

D. Whisky

These absorbance spectra may, naturally, be observed in any solution, but what tells two substances apart is where they lie, and their intensities. We will be looking at whiskies in an attempt to tell them apart, but also to try to figure out how much caramel (E150) they contain. E150 is a common additive used for mimicking the color gained by aging in oak casks.

In a paper by Boscolo et al. [2], a method of estimating caramel content by absorption is presented. This method involves measuring absorbance at 210 nm and

282 nm. Our cuvettes had a light path of 1 cm, equivalent to the one used by Boscolo et al. Their empiric formula for caramel content is

$$CC = (A_{282} - A_{210}/4.2)/CA_{282} \qquad (6)$$

where CC is the caramel content, A_x is the measured absorbance at x nm, and $CA_{282} = 8.0$ L/(g cm) is the absorptivity of caramel at 282 nm.

Figure 2: The Ocean Optics Flame miniature spectrometer with the Ocean Optics UV-Vis absorption sampling system attached.

III. Setup and execution

For the observation of emission spectra a Ocean Optics Flame miniature spectrometer, a grating spectrometer, is used. To minimize unwanted light, an optic fiber is attached to the spectrometer and pointed at the desired source. For the absorption spectra, a Ocean Optics UV-Vis sampling system is attached to the spectrometer, as seen on figure 2. To calibrate the device, a cuvette with demineralized water is inserted into the slot in the sampling system. Using the purpose-built software Ocean-View, the spectrum, with the bulb of the sampling system turned on, is recorded as the background. The software then automatically subtracts this spectrum from later observed spectra, showing only the discrepancy as an absolute value.

The CCD in our spectrometer is a Sony ILX511B with 2048 pixels.

A. Calibration

As described before the device that converts the actual photons into a measurable signal is an array of pixels (CCD), where, due to the geometry of a diffraction spectrometer, the position of the hit CCD pixel corresponds to a specific energy/wavelength. Figure 4 shows the raw recorded signal from a spectral lamp filled with Hg.

We are using spectral lines to calibrate since they have well-known and well-documented positions, e.g. through the NIST database. As seen from figure 4, some lines are more easily picked out than others; the sharp, intense and spatially separated, ie. those marked by red x's.

From their relative intensities and separation, we have, consulting the vast and precise catalogues of NIST [6], deduced which transitions and corresponding energies, are responsible for the peaks. The CCD array then tells us, which pixel has been hit, allowing for a fit to the deduced wavelength.

IV. Results

In the following we present our results regarding the calibration of the CCD, the solar spectrum and the absorbance of UV-VIS light by 15 separate whiskies.

A. Calibration

Measuring spectral lines from H_2, He, Ne, Hg and Ar a wavelength-calibration is obtained, as shown on figure 3. This figure also displays the stock calibration, which seems to be in agreement. Our calibration was done to a 2nd-degree polynomial fit, while the stock is a 3rd-degree polynomial [3]. The reason for this is to avoid higher-order instabilities on extrapolation outside our range of data.
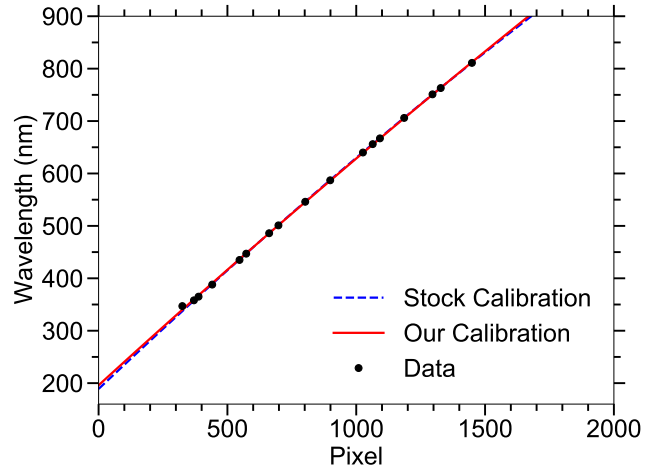

Figure 3: Our calibration in comparison to the stock calibration.

Our calibration yields the following parameters to a 2nd-degree polynomial $f(x) = \alpha_0 + \alpha_1 x + \alpha_2 x^2$.

$$\alpha_0 = (196 \pm 2) \text{ nm} \qquad (7)$$
$$\alpha_1 = (0.486 \pm 0.004) \text{ nm} \qquad (8)$$
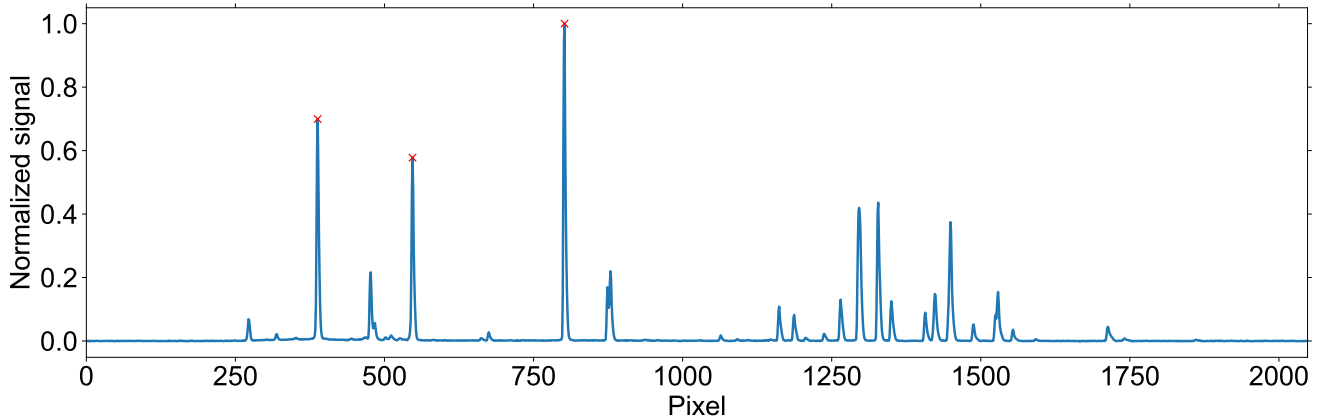$$\alpha_2 = (-1.6 \pm 0.2) \times 10^{-5} \text{ nm} \qquad (9)$$

Figure 4: Raw data of Hg spectral lines measured from a spectral lamp. Red x's indicate the more separated peaks used for calibration

B.   Whisky analysis

Note: Time-constraints unfortunately didn't make it possible to take calibration spectra as well as the absorption spectra. Therefore the following section was done using the stock calibration, but could have been calibrated using the described technique.

On figure 5 the UV-VIS spectrum of 15 different whiskies is seen together with a control, a sirup solution. The sirup solution was simply made by dissolving sirup in water until a comparable absorption was obtained, and is solely used for a qualitative comparison. As seen, the sirup spectrum shares characteristics with the whiskies. Using the method developed by Boscolo et al. [2], we obtain a concentration of E150 of around 0.6 g/L for all whiskies as well as the measured sirup solution. Note: with unknown uncertainty since the uncertainty in the empiric formula are unknown, but we estimate it to be around 0.1 g/L.

In an effort to tell the whiskies apart we quantify the differences in absorbance spectra by using an absorption factor, A-factor, which is found by integrating the absorption over the interval from 290 nm to 390 nm as indicated on the figure by the vertical dashed lines. Figure 6 is then a zoom of the previous figure on this interval. As seen the whiskies divide into 3-ish groups depending on their absorption. Note: there are two peaks around 328 nm and 337 nm which seem to vary in amplitude together with the surrounding shoulder to the largest peak at 270 nm. Matching the ratings of the whiskies, democratically given on the website `whiskybase.com`, with their A-factors gives rise to figure 7. Furthermore, we have matched the A-factors and prices of whiskies, in figure 8.
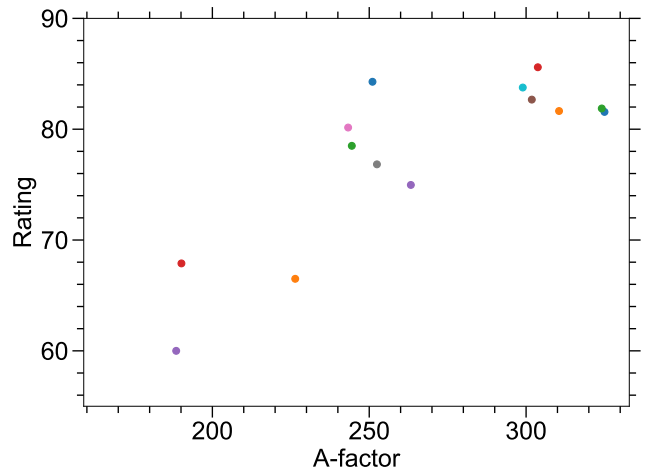

Figure 7: Absorption factor vs rating. Ratings from `whiskybase.com` and out of 100. Possible trend seen, also the three groupings are visible.
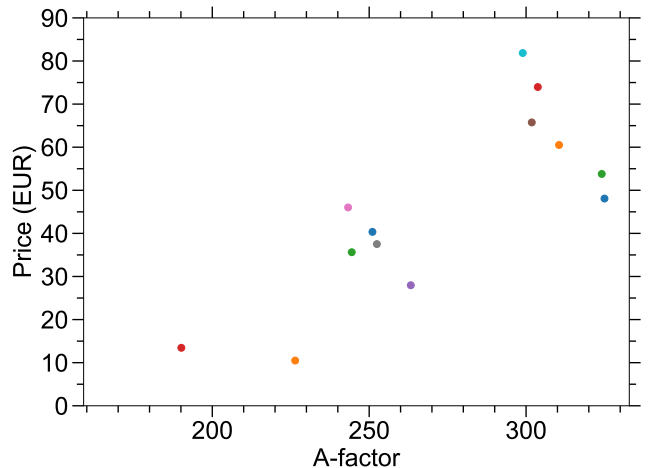

Figure 8: Absorption factor vs. price. Pricing from a number of danish online stores and `whiskybase.com`. Possible trend seen, also the three groupings are visible.
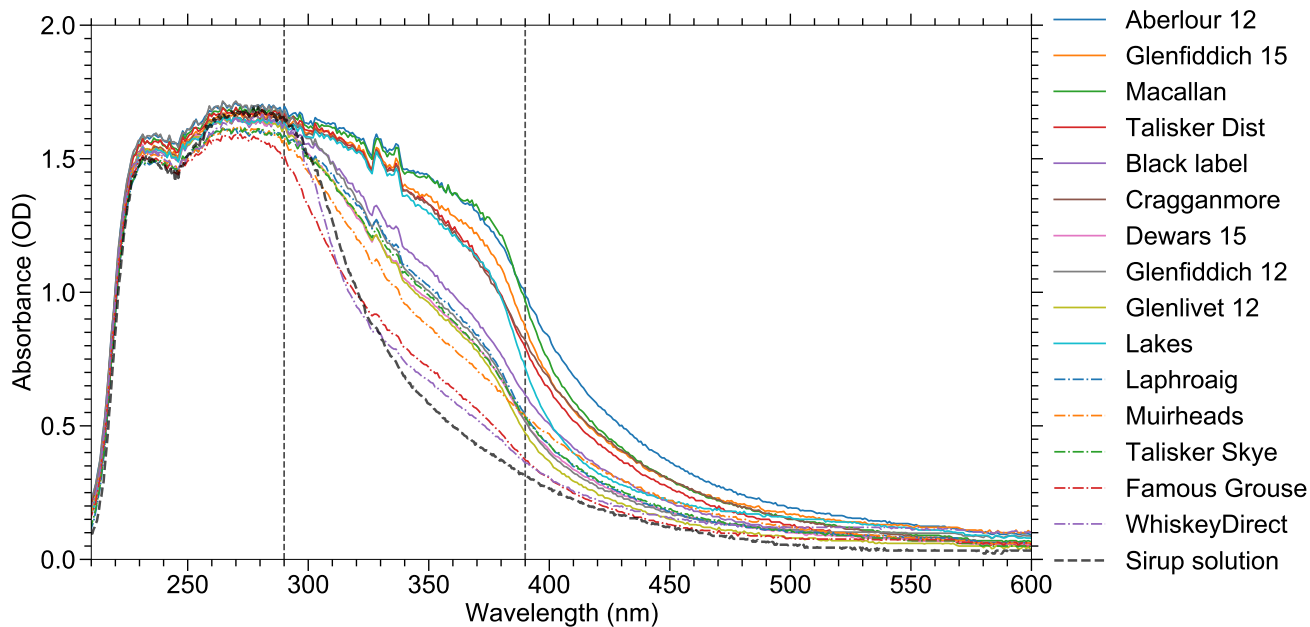
Figure 5: This figure shows absorbance in UV-VIS of 15 different kinds of whisky together with a diluted sirup solution.
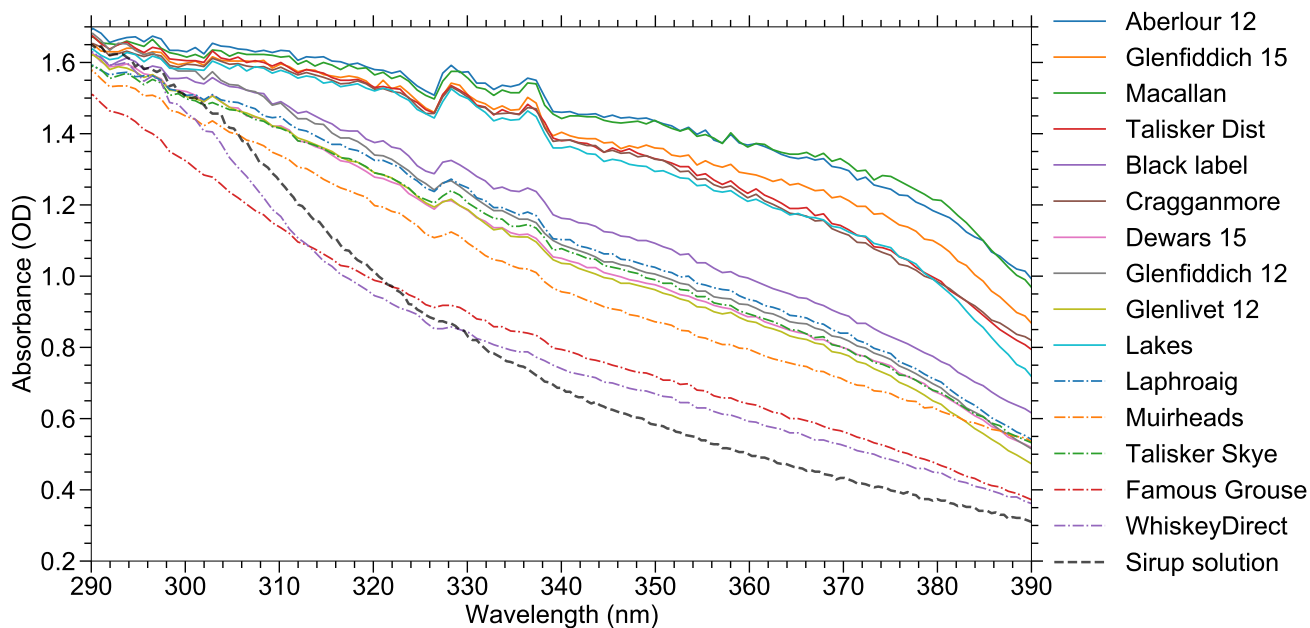

Figure 6: View of the integration interval used for the A-factor of the figure above.
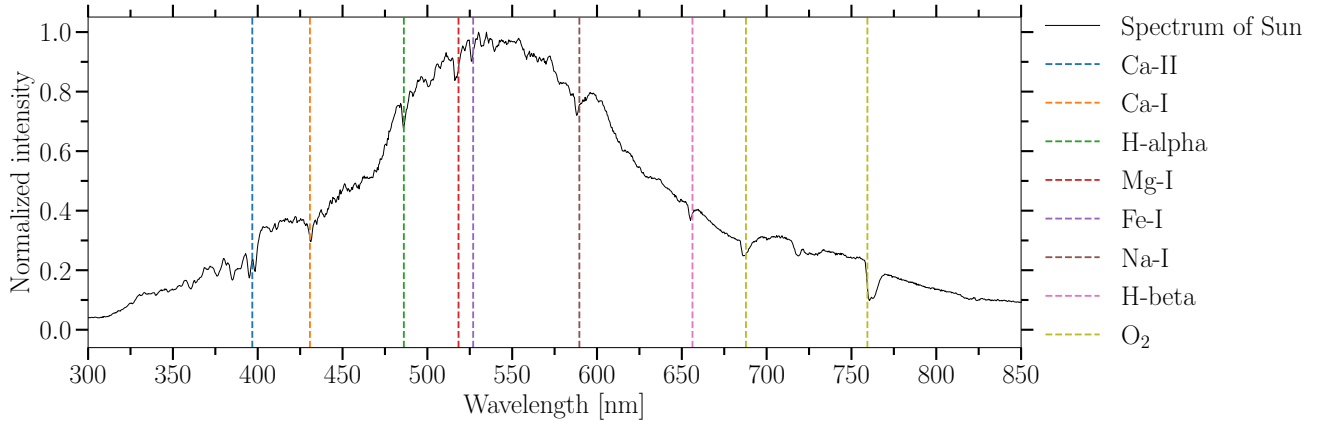
Figure 9: The solar spectrum, as recorded on a cloudy day in Aarhus. For this plot, our own calibration method has been used. Several Fraunhofer lines are also shown in arbitrary colors.

C. Solar spectral lines

Figure 9 shows the solar spectrum as recorded on a cloudy day in Aarhus. For this dataset, the aforementioned calibration is used. The figure also contains several *Fraunhofer lines* [10], corresponding to solar and telluric absorption lines.

V. Discussion

A. Calibration and Solar spectrum

As evident in figure 9, we observe several absorption lines when recording the solar spectrum. Upon comparison with the well-known Fraunhofer lines, which matches well with the sudden dips in intensity, we can affirm our calibration method. Also evident is the fact, that our recorded spectrum differs from the overall shape of the characteristic Planck curve. This we attribute to the fact that the efficiency of a CCD pixel depends on the wavelength of the incident photon [12]. As noted, the CCD used is a Sony ILX511B, which has a non-constant response curve as seen on figure 12 in the appendix. Since the spectrometer has not had a irradiance/intensity calibration a number of 450 nm photons will give a much larger signal compared to the same number of 600 nm photons. This distorts the shape of the signal, thus distorting the expected Planck curve.

The response curve, however, shouldn't affect the calibration, as the positions of the spectral lines are unaffected. This just makes it a bit more difficult in locating the lines in NIST, as their intensities may not align with ours. If the NIST database *had* supplied an intensity, that was normalized across all their used sources, we could have made a plot of the response curve for our specific CCD – in other words done an irradiance/intensity calibration.

B. Whisky

Aging whisky in oak casks for extended time leads to the spirit extracting phenolic compounds from the wood, which leads to its golden colour [2]. Aging, however, is an expensive process, so to mimic the golden color E150 is often added to younger whiskies. This is why groups like Boscolo et al. have developed methods for determining the caramel (E150) concentration in aged spirits.

Unfortunately we didn't have E150 at hand, so sirup was used in place. The two share a common step in production: heating of sugars, which in turn produces the characteristic caramel compounds; caramelans, caramelens, caramelins [5][8].

Obviously whisky isn't as sweet as the very sweet sirup solution, but by looking at the minor contribution of glucose to the absorption spectrum (see figure 11 in appendix), it is clear that the signal must be from something else. The whisky "The Famous Grouse" declares on the label that it contains E150, so considering the striking likeness of that signal and the sirup signal, we can conclude that our sirup solution is a fair representation at these wavelengths. This would also seem to indicate, that the rest of the contents, e.g. 40% alcohol, does very little to the UV-Vis spectrum for a young, mass produced whisky like "The Famous Grouse".

However, even though all the signals share similarities to the sirup and the Boscolo et al. method implies so as well, we cannot conclude that E150 has been added. In the process of toasting barrels, which all scotch whiskies age in for a minimum of 3 years [13], the polysaccharides of the wood breaks down to monosaccharides which upon heating go through the same process of caramelization as E150 and sirup, so upon storing the whisky in a toasted barrel these caramel-compounds are transferred to the final product [8].

Even if the barrels haven't been toasted, many of the phenolic compounds absorb light around the same peaks

(eg. o-Cresol [7] and Guaiacol [1]). This fact raises questions regarding the Boscolo et al. method.

Furthermore, there are some legal implications regarding whether or not all the whiskies actually have had E150 added, since per EU law, all additives must be visible on the label, and E150 is not stated for most of the tested whiskies. Therefore, in order to determine which compounds contribute to the signal, thus constituting the observed A-factor, it would be preferable to determine the individual concentration of the compounds, eg. via gas chromatography-mass spectrometry. Through such an analysis we would be able to determine if the proposed method by Boscolo et al. works.

This would be especially interesting with regards to the two peaks around 330 nm, since there seems to be some correlation between the overall size of this shoulder of the main peak - ie. the A-factor, and both the rating and the pricing of the whisky. Our data definitely does not reject the possibility, that the molecule(s) responsible for the absorbance in this area improves the overall taste of the whisky. A complication might arise with the introduction of very peaty, smoky whiskies. Especially the Laphroaig, a notoriously peaty whisky, has received an extraordinary score on `whiskybase.com` while exhibiting a relatively low A-factor. One explanation might be, that the addition of peaty compounds is such, that, for some people, this might equal out the lack of the molecule(s) that are responsible for the A-factor, which seem to set other whiskies in higher esteem.

With regards to the A-factor vs. pricing plot, there seems to be a correlation suggesting that the molecule(s) responsible for the A-factor require a more expensive process - perhaps longer aging or aging in a cask of a particularly special kind of wood.

VI.   Conclusion

With the factory-made instrument, the Ocean Optics Spectrometer Flame and its attachment, we have scrutinized the spectral lines of several sources. The emission lines of several gasses in a gas-discharge lamp served to calibrate the input from the CCD, which then led us to identify several Fraunhofer lines in an observed solar spectrum. Also, the absorption of UV-Vis light was investigated for 15 scotch whiskies. Though we were not able to discern individual molecules or compounds, nor differentiate between varying additions of E150, the different whiskies divided into 3 main groups based on their absorption between 290 and 390 nm. This lead to the introduction of the A-factor, the integral beneath the curve for this interval, which was compared to the rating and pricing of each whisky. Though nothing set in stone can be declared, our findings does not disavow the possibility, that the molecule(s) responsible for the absorption of light with these wavelengths contribute to the price and esteem of a whisky.

References

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[3] *Flame Miniature Spectrometer User Manual.* See p. 59. A Halma Company.

[4] Christopher J. Foot. *Atomic Physics.* Oxford University Press, 2005.

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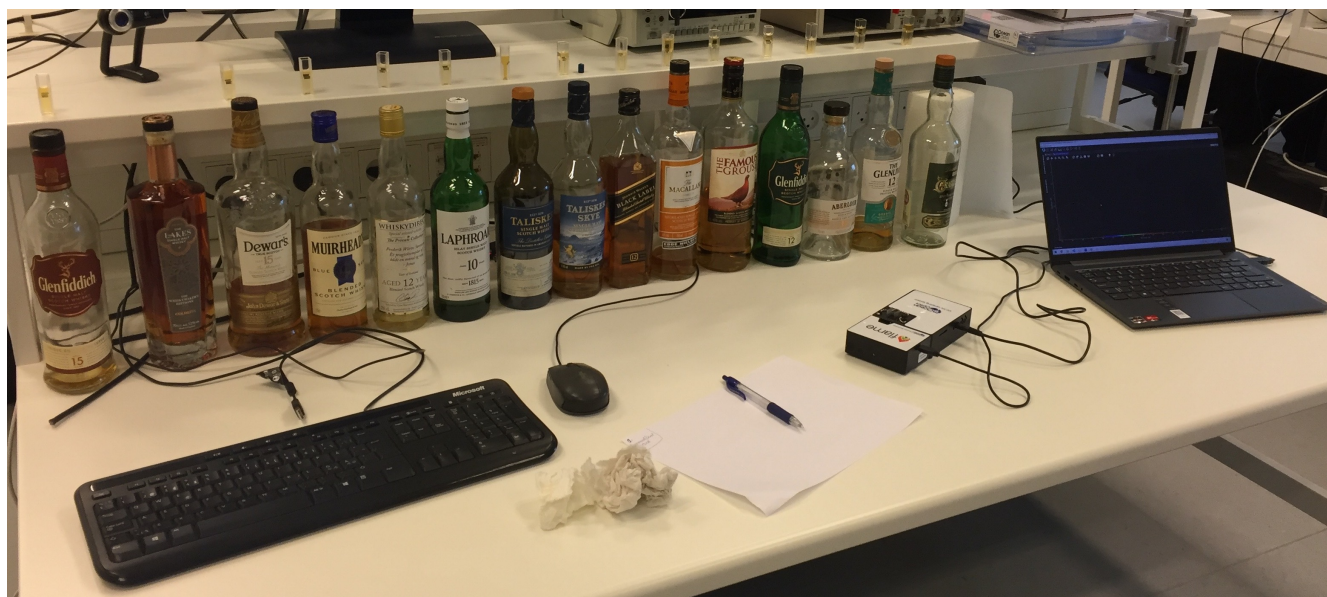
VII.   Appendix

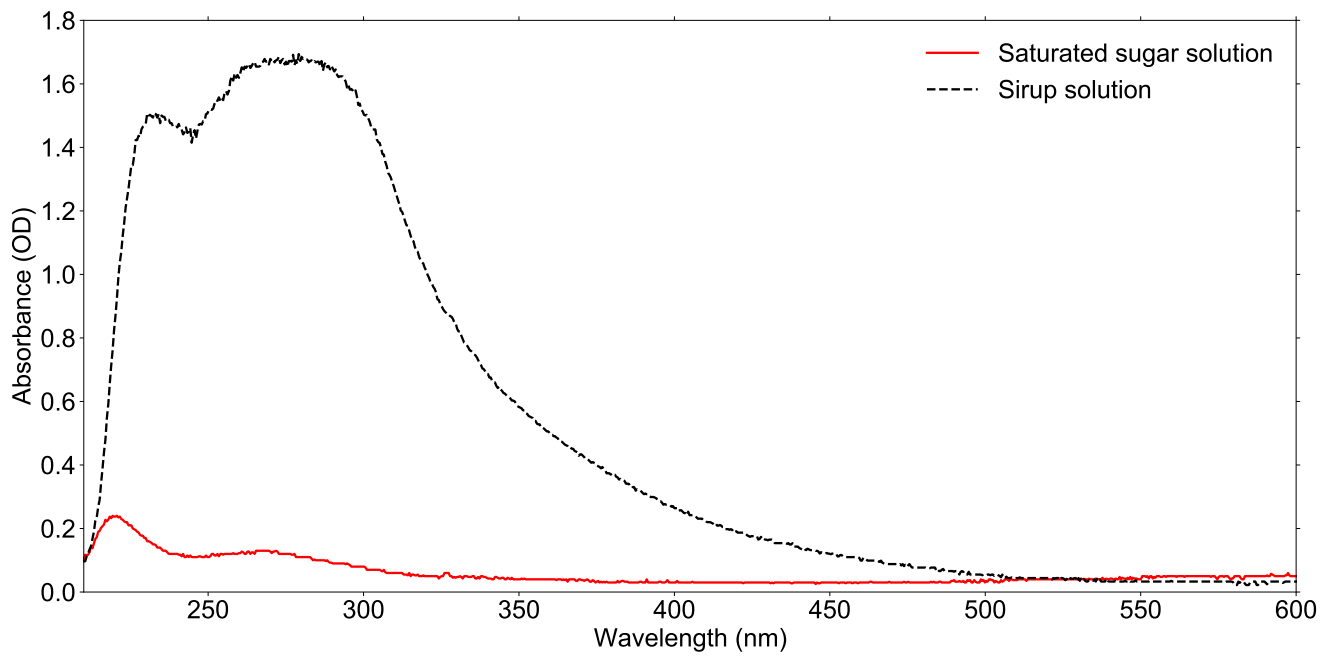Figure 10: The 15 sampled whiskies next to the experimental setup. Just another day in the lab.

Figure 11: An absorption plot of a saturated sugar solution together with the used, unsaturated, sirup solution
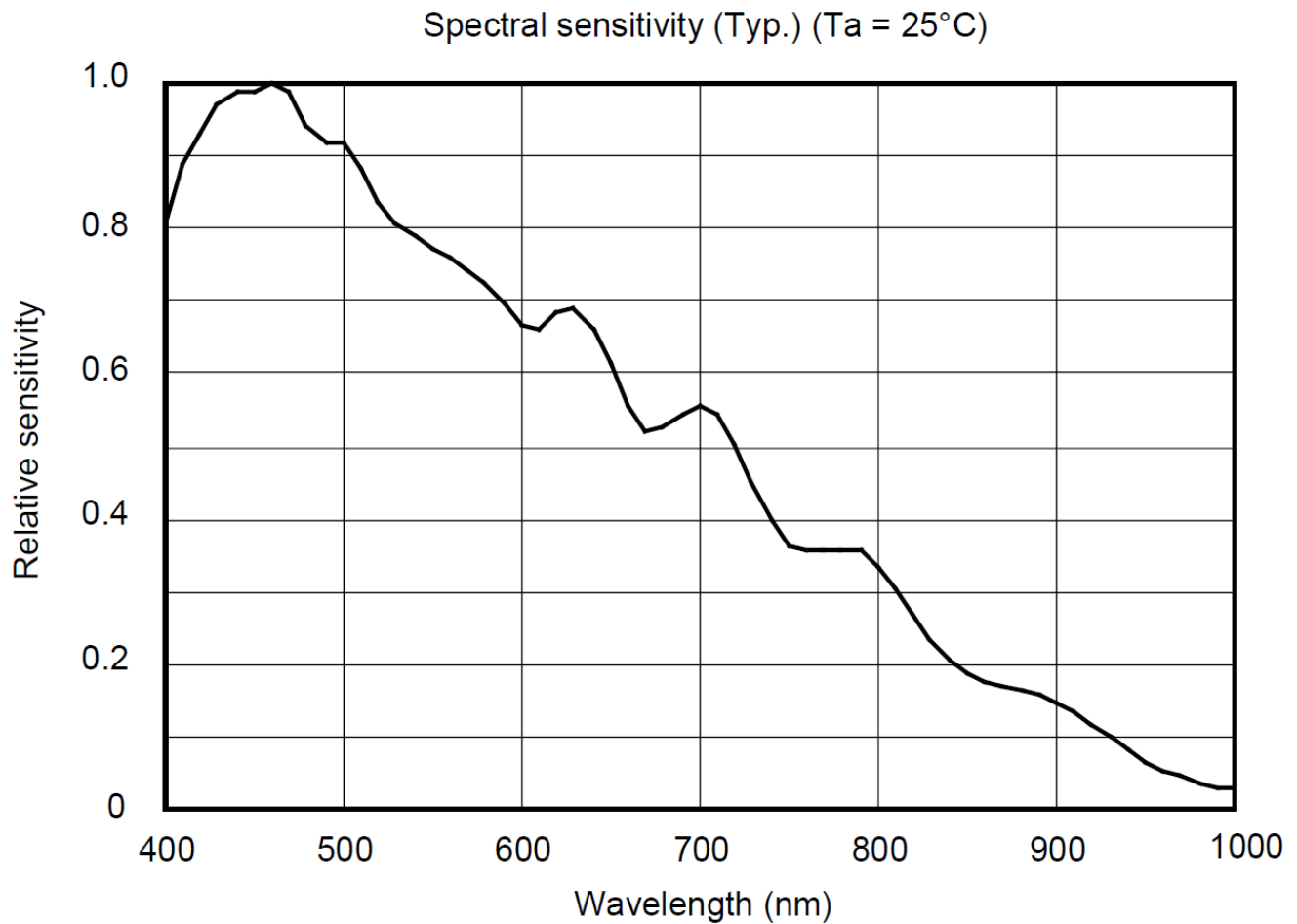

Figure 12: Typical spectral sensitivity of a Sony ILX511B CCD chip. Source: Sony spec sheet
spectralproducts.com/pdf/ILX511.pdf