

DESIGN OF AN ADVANCED DIGITAL HUMAN EYE AND IT VARIOUS INDUSTRIAL APPLICATIONS : PHOTOELECTRIC REFLECTANCE METER (ASTM D 6468)

Pioneer of the Photoelectric Reflectometer

One of the most used senses in our daily lives is sight. In fact, the human eye is able to qualitatively identify around one million different colors but struggles to commit them to memory due to different viewing angles and surrounding lighting affecting color intensity. During the twentieth century, researchers have sought ways to develop a machine to optimize color sensing and set forth a color standard, eventually painting the creation of the reflectometer.[1]

According to a research journal by the National Bureau of Standards in 1940, one of the first reflectometers was created by Richard Sewall Hunter to visually measure the relative reflectance or transmittance of light value of a sample using a shifting mirror as seen in Figure 1. This particular instrument was designed to be simple, created by inexpensive, widely available materials, and applicable to a broad range of testing surfaces. One of their users, the Committee on Standardization of Tests of the Porcelain Enamel Institute, inquired if the instrument could be photoelectric rather than visual to enhance their own study of porcelain-enamel surfaces. In response to this request, the Photox 0°, 45° reflectometer was invented with two adjusted barrier-layered photocells connected to a galvanometer to act as a non-human eye light detector measuring the percent of light reflectance or transmittance in Figure 2. Around the same era, it was fathomed that color was understood by the human eye to be composed of three primary colors: red, green, and blue, otherwise known as the tristimulus values. Thus, colored-glass (commonly amber, green and blue) were introduced as filters for the reflectometer to obtain higher photoelectric precision and color difference and assist it in becoming a digital human eye in tristimulus colorimetry and spectrophotometry.

Hunter's innovation was intended to be industrially multi-purpose, ranging from measuring the opacity of paints to cleaning power of soaps to bleaching strength of cloth.[2] His legacy continues on as his Photox 0°, 45° reflectometer would be improved upon over the next few decades as a Koehler Instrument Company's new Digital Reflection Meter and still be ubiquitous across various fields, especially the petroleum and food industries.

ASTM D6468

One key application of the Koehler Instrument Company new photoelectric reflectance unit can be found in the petroleum industry where it can investigate the thermal stability of distillate fuels as outlined in ASTM D6468. The thermal stability of a fuel measures a fuel capacity to endure high thermal stress before experiencing self-deterioration. Color changes, presence of solid deposits, and alterations in physical or chemical properties are associated with deterioration that could potentially decrease fuel efficiency, interfere with machine operations, and increase financial costs.[3]

The test method involves heating distilled fuels with flash points more than 38°C to 150°C with limited air exposures to replicate thermal stresses from engine or fuel system environments, 90 minutes of aging and cooling, vacuum filtering insoluble particles, and measuring the light reflectance

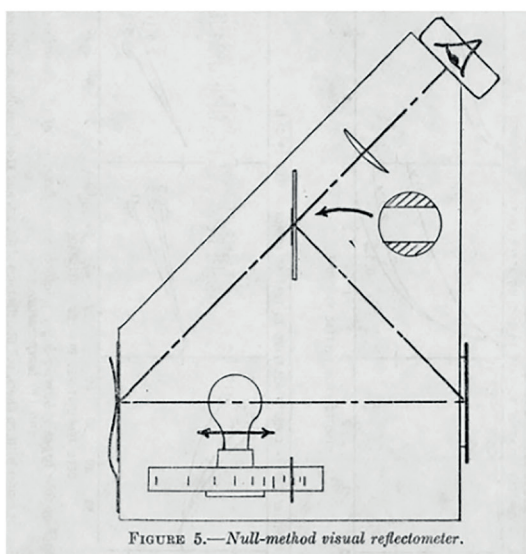


Figure 1. Sketch of Richard Hunter's visual reflectometer [2]

of these particles using K 30700, Koehler Instrument Company's reflectance unit.[4]

Figure 3 showcases the K30700 Reflectance Unit from Koehler Instrument company inc. with a green-filtered search unit Y compatible with the aforementioned testing method. The Koehler Instrument Company would be calibrated with a black glass standard to set a "zero" percentage reflectance benchmark while a porous filter paper would act as the



Figure 3. Picture of Koehler Instrument Company, Inc.'s Reflectance Unit

100% reflectance value. The procedure listed in ASTM D6468 requires 100mL of diesel fuel to be filtered at 27kPa before separated into two 50mL tubes and placed in a 150°C heating

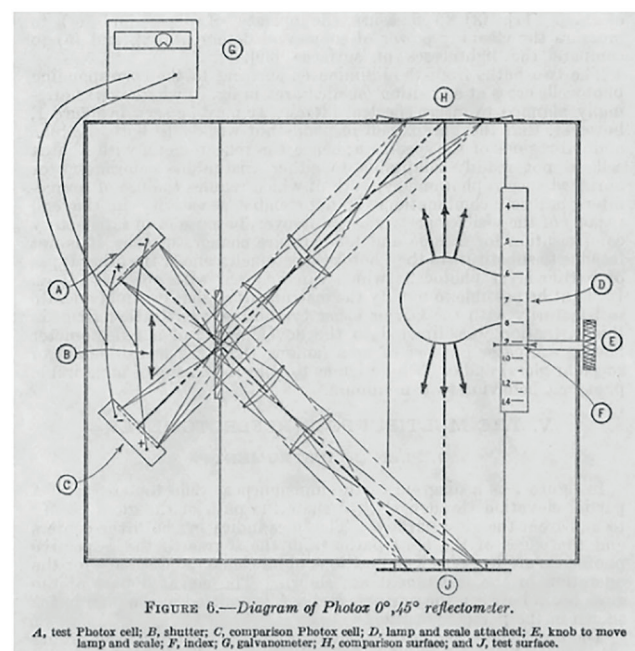


Figure 2. Sketch of the Photox 0o, 45o reflectometer [2]

bath. After aging for 90 minutes in the hot bath, the diesel tubes were left to cool until room temperature before being filtered again. The filter paper in the distillation apparatus containing insoluble particles was carefully retrieved, placed on top of a stack of ten clean filter papers, and positioned face-down on top of the search unit to ascertain the percentage of light reflectance. Figure 4 displays the strong, positive correlation between relative stability and percent reflectance for the Y/W search units, implying the increasing thermal stability of a fuel with a higher percentage reflectance. Both the Y search unit (containing insertable tristimulus filters) and the W search unit (containing a built-in blue tristimulus filter) are acceptable for ASTM 6468, but varying interpretations of the results with the difference in light wavelength of the colored filters.[4]

Photoelectric Reflectance in the Food Industry

Carcinogens in Potato Chips

At the start of the twenty-first century, acrylamide (AA), a potential carcinogen, was abundant in processed foods, including potato chips, bread, and coffee. Hence, in 2016,

TABLE X1.1 Interpretation of Results

Relative Stability	Y Search Unit with Green Filter % Reflectance	W Search Unit % Reflectance
Decreasing Stability ↓	100-90	100-85
	89-80	84-71
	79-70	70-62
	69-60	61-53
	59-50	52-32
	49-0	31-0

Figure 4. Table relating percent reflectance to stability for Y and W search units in ASTM D6468 [4]

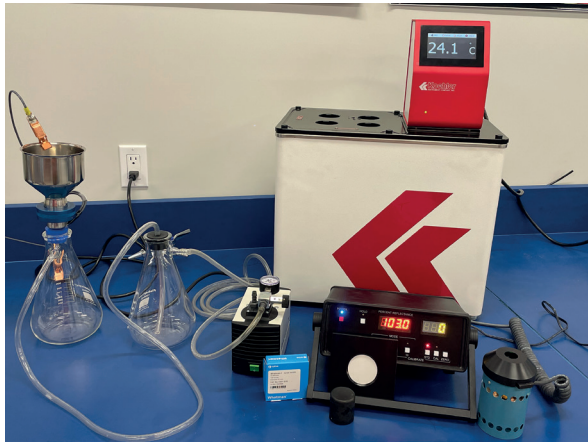


Figure 5. Full experimental set up for Astm D6468

Qinqin Hu et al. affiliated with Zhejiang University and the University of Arkansas introduced a time and cost-effective method of detecting AA in foods using colorimetry. In the study, it was noted that the thiol chemical functional group in glutathione (GSH) is capable of aggregating gold nanoparticles (AuNPs) and causing a red to purple color change. However, with the addition of AA, GSH is consumed by the AA compound (known as a thiolene Michael addition reaction) with the assistance of the catalyst TCEP and hinders the aggregation of AuNPs. Figure 5 displays the difference between the aggregation of AuNPs with just GSH and an GSH-AA adjunct. On the right side, the thiol group (SH) on GSH absorbs the surface of the AuNPs, decreasing the surface area of the AuNPs and causing an overall purple hue solution. On the left side, AA molecules are represented as orange triangles attaching themselves to the thiol group of GSH, leading to GSH-AA adjuncts to depart from the AuNPs and remain a red hue solution. Hence, the concentration of AA in a food sample could be discerned through a color difference initiated by the aggregation level of AuNPs.

Hu et al. experimented with various mixtures with or without AA (extracted from store-bought potato chips), GSH, or TEMP levels and analyzed the absorbance of light of these mixtures at different wavelengths. Figure 6 displays the UV-vis absorption spectra of eight different mixtures and the corresponding solution colors. Line 5 indicated the strongest aggregation of AuNPs with the highest absorbance peaks and the most purple solution color without the addition of AA. Meanwhile, the absorbance levels of mixtures with the presence of AA was only 60% of the mixtures with AA at the second peak (implying less aggregation intensity) and the mixtures had a redder hue. Visual representation of the AuNP clusters could be seen in Figure 7. Figure 7b represents the dispersion of AuNPs of Mixture 8 (AuNPs-GSH-AA mixture with TCEP); Figure 7c highlights the most concentration of AuNPs in Mixture 5 with no AA addition; Figure 7d shows a middle ground dispersion of AuNPs in Mixture 7 (AuNPs-GSH-AA mixture without TCEP). Considering the clear color differences, absorption spectra, and cluster photography of AuNPs with and without AA, it was concluded that this colorimetric method of identifying the presence of AA in potato chips was successful and could be applicable to the safety testing procedure of processed foods.[5]

Predicament of White Wine Taste

In 2015, Soo Chung et al. from Seoul National University quantified the taste of twenty-three different white wines through ascertaining the correlation between RGB color changes in chemically dyed beads soaking in wine solvents to the chemicals responsible for taste in wine. Chung et al. aimed to develop a method to predict the grade of sweetness, sourness, and astringency within a wide sample size of white

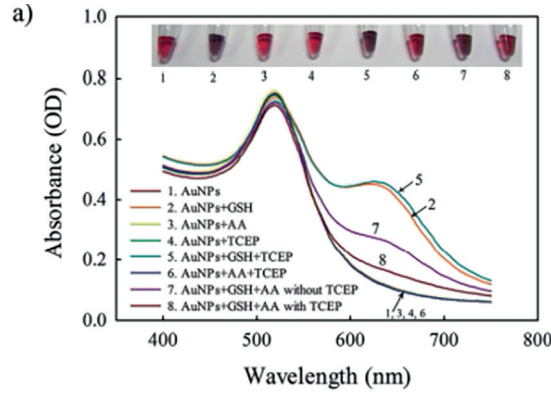


Figure 6. Absorption spectra of AA and/or GSH and/or TEMP mixtures [5]

wine. Using high performance liquid chromatography, they attributed sucrose, glucose, and fructose to be the contributors of sweetness and labeled citric acid and malic acid (amongst many more acids) to be responsible for the sourness of the wines. Meanwhile, tannin and lignin test kits were used to measure the amount of phenolic compounds in each wine sample to determine the corresponding tannin values. In the experiment, eight types of chemical dyes (alizarin, calconcarboxylic acid, cresol red, crystal violet, fluorescein, methylthymol blue, phenol red, and xylenol orange) were applied onto polystyrene microbeads before being placed into a sensor array well in a buffer solution and submerged in white wine samples. Peering down at the sensor array was a charged-coupled device (CCD) camera to capture images of the array and record the RGB value changes in each well five minutes before and five minutes after the addition of wine. Figure 8 illustrates the setup of this process while Figure 9 displays obvious color changes in the control dye-solutions after the addition of three different white wine samples.

Afterwards, the relationship between the taste-dependent chemicals and RGB color changes was analyzed via an absorption spectrum using the dye-mixtures and varying concentrations of the taste-dependent chemicals. The strength of RGB color change (denoted as the coefficient of determination, R²) to each taste-dependent chemical of each dye is graphically summarized in Figure 10, noticeably all dyes had unique RGB numbers for each chemical.

With the gathered color data above, a principal color analysis

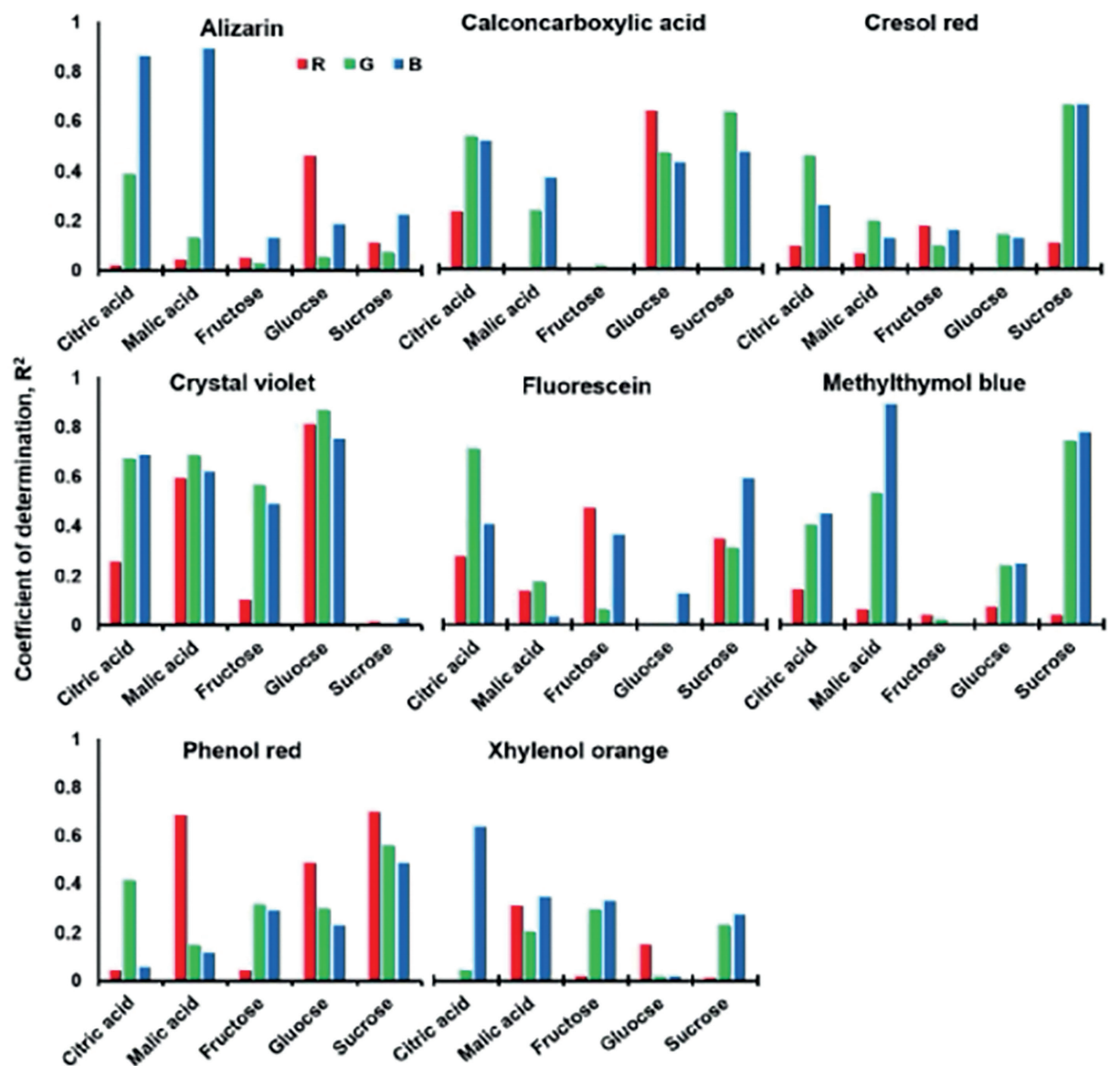


Figure 10. R² vs. taste-dependent chemicals graphs of each chemical-dyed microbead [6] (PCA) was performed. PCA creates principal components (PC)

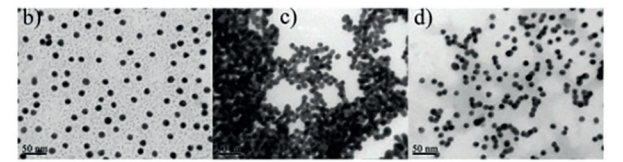


Figure 7. Microscopic view of AuNPs clusters [5]

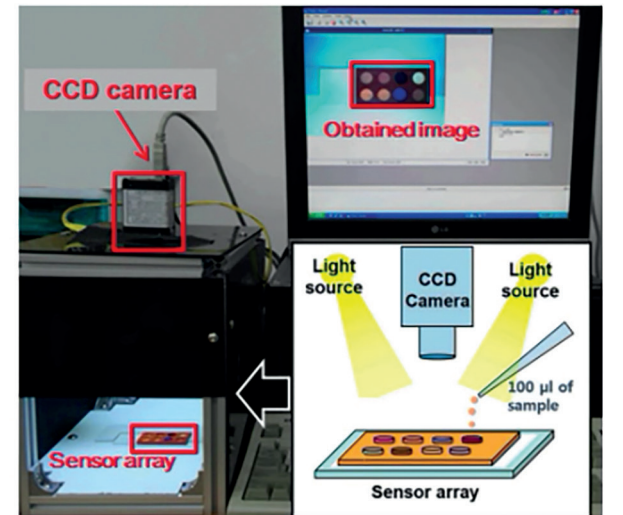


Figure 8. Setup of CCD camera and sensor array [6]

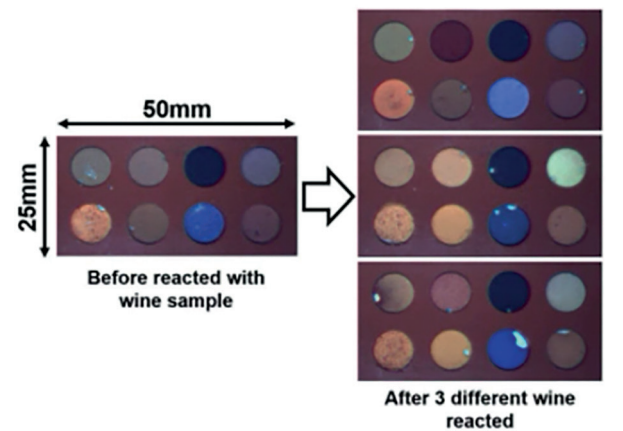


Figure 9. Changes in microbead's RGB colors [6]

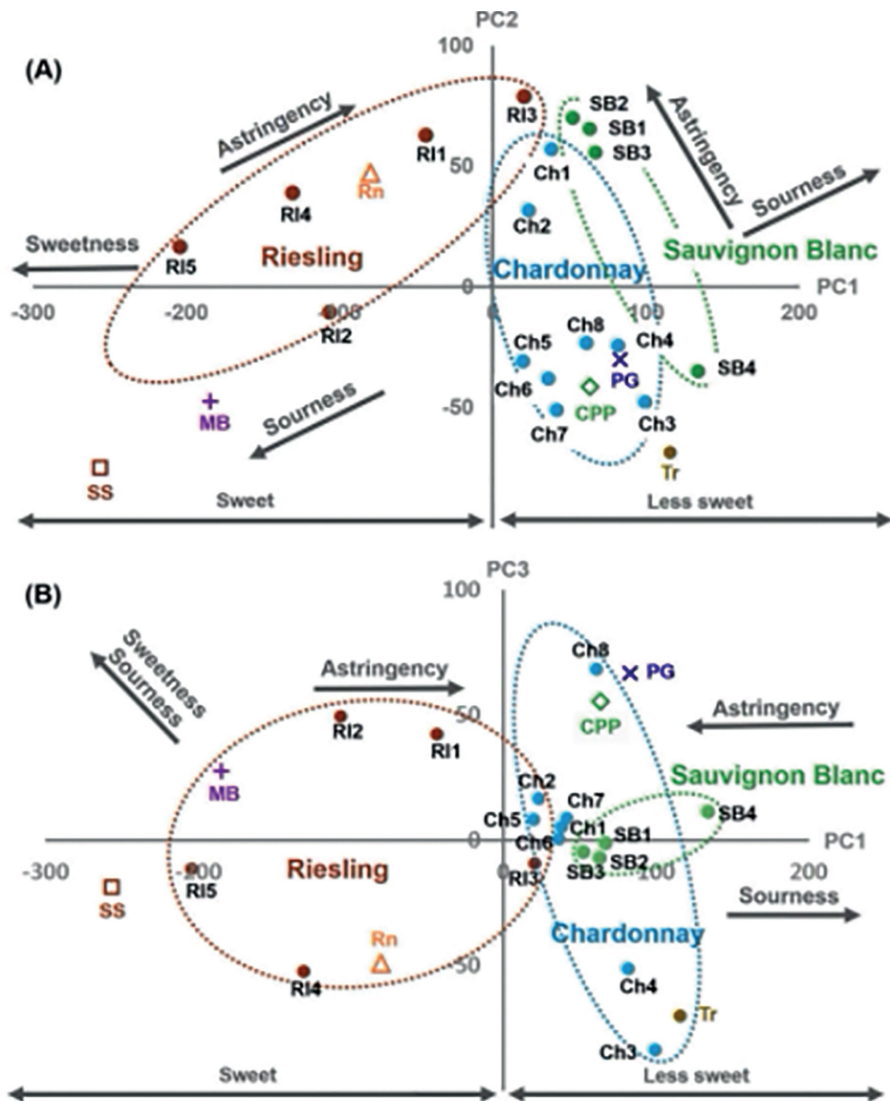


Figure 11. Principal Component Analysis (PCA) graphs. a) PC2 vs. PC1 b) PC3 vs. PC1 [6]

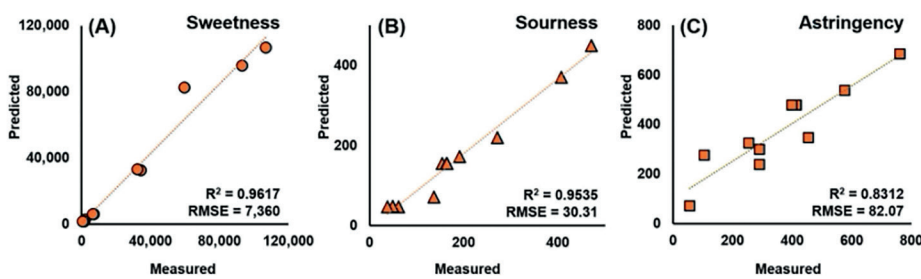


Figure 12. Graphs of predicted vs. measured values for sweetness, sourness, and astringency [6]

that sum up the most common variables amongst all the color values in these dyes and plots them with each other to see running trends within the types of white wine tested. Figure 11a illustrates the plotting of PC 1 (a summation of 55.96% of all variables in the sampling) with PC

2 (14.94% of variables of the sampling not included in PC 1) with noted arrows representing the trend of astringency increasing along the +y-axis, sweetness increasing along the -x-axis, and sourness increasing farther away from the origin in the first and third quadrants. Figure 11b illustrates the plotting of PC 1 with PC 3 (11.66% of variables of the sampling not included in PC 1 or 2) with noted arrows representing the trend of increasing astringency nearest to the +y-axis, sweetness increasing along the -x-axis, and sourness increasing along the +x-axis. Clusters of samples with the same grape variety are also seen and are highlighted and grouped in different colors (Riesling in brown, Chardonnay in blue, and Sauvignon Blanc in green).

Lastly, Chung et al. used an artificial neural network model (ANN) to predict estimated levels of sweetness, sourness, and astringency with the given color data and plotted them against their measured values of the wines. The plots of each taste element that garnered the highest coefficient of determination R^2 (measurement of linear strength correlation between two values) and the lowest calculated root mean square error of prediction RMSEP was deemed the most favorable one. Figure 12 displays the color data's predicted values compared actual values with high R^2 values of 0.96, 0.95, and 0.83 (extremely close to the perfect 1.0 value) and low RMSE values of 7,360, 30.31, and 82.07 for sweetness, sourness, and astringency, respectively. The formation of a nearly linear relationship between the predicted and actual values for the listed taste elements reflects the accuracy of the RGB color data set and versatility in generating trendlines for the sweetness, sourness, and astringency of white wines. Consequently, colorimetric sensing of taste has potential to estimate taste qualities in wine and be an alternative tool in catering towards customers' taste preferences.[6]

Conclusion

Whether it is examining the thermal stability in fuels, carcinogens in potato chips, or the taste elements in white wine, the Koehler Instrument Company's photoelectric reflectance unit proves its vital, multi-faceted role in society. From the start of the twentieth century, the notion of using simple manipulation of light through colored lenses already opened doors to a palette of applications. Nonetheless, we continue to use simple colors solutions to solve challenging problems, hopefully on a grander and more successful scale.

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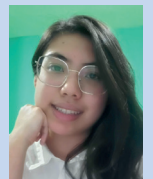
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