J. Inst. Brew., November–December, 1992, Vol. 98, *pp.* 497–504

COLOUR DETERMINATION OF BEER USING TRISTIMULUS VALUES

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Received 30 January 1992

The derivation of tristimulus and chromaticity values for beers, using transmission measurements, is discussed. Chromaticity values indicate that the majority of beers have colours which resemble those represented by the EBC colour scale. However, the dilution of dark beers for colour analysis, according to Recommended Methods, leads to non-standard colours. The colour adjustment of beers, using colouring agents, can also produce colours which deviate markedly from the standard EBC colour range. On this basis, the adoption of tristimulus measurement for quantification of beer colour is proposed. A method for obtaining tristimulus values of beers, based on transmission measurements at 5, 6 or 7 wavelengths, gives results comparing favourably with those from standard procedure, which requires transmission measurements at 5 nm, 10 nm or 20 nm intervals across the entire visible spectrum.

Key Words: *Analysis, beer colour, colouring agent, computation, spectrophotometry.*

Introduction

The modern consumer expects consistently high standards of quality in foods and beverages. After inspection of packaging, visual appearance of the product within is the first indication to the consumer of its wholesomeness. This is especially true of beer, where reproducible foam and colour are key quality targets.

Colour arises from the ability of certain wavelengths of light to induce a physiochemical response in light-sensitive cone cells in the retina of the eye. These cells are individually sensitive to red, green or blue light. The brain then combines the three responses in a way that is meaningful for most people, in terms of what is thought of a 'colour'. Any hue, shade or tint that the human eye can perceive can be thought of, therefore, as an admixture of varying proportions and intensities of red, green and blue. It has been estimated, by Judd and Wyszecki[15], that the human eye can distinguish between ten million such individual hues.

Because colour lacks any obvious physical existence, it follows that it is not possible to make a direct measurement objectively. Any colour determination performed in the laboratory, or in a process control environment, must be either based on a visual comparison or inferred from light absorbance, transmission or reflectance data.

Standard Illuminants

The colour of a material will appear to change, depending on whether it is viewed under tungsten or fluorescent light, under average daylight or under strong sunlight. Consequently, the energy of the illuminating light source, across the visible spectrum ("colour temperature"), must be taken into consideration when evaluating colours. A number of standard illuminants have been defined by the Commission Internationale de l'Eclairage (CIE), the international committee responsible for overseeing standards in light and colour analysis. Each illuminant is described in terms of a series of intensity values, at regular wavelength intervals over the range 300 nm to 900 nm and represents a standard example of light from a given source. Colour temperatures for a number of CIE Standard Illuminants, and their physical equivalents, are given in Table I. The spectral power distributions for several of the more commonly used standard illuminants are illustrated in Figure 1.

EBC Colour Scale

Over the years many methods have been devised to quantify beer colour. The first series of colour discs, the "52" series, was developed by Lovibond in 1893[17], whereby beers were assigned a value based on comparison against a set of numbered slides of standard colours. A revised set of slides, with subtly altered colour characteristics, was proposed by Bishop[2] in 1950 and, subsequently, manufactured by the Tintometer Company, England. These were ultimately adopted as the EBC Method for the analysis of beer colour in 1951. Although the use of Lovibond discs remains the recommended procedure for the colour analysis of worts prepared during the course of malt analysis[14], problems are frequently encountered with variation in operator performance, ocular fatigue, variation in colour of light sources and discs due to ageing, and variation in the colours of new discs corrected for Illuminant C. The cumulative effect is the

TABLE I. Colour temperatures and physical equivalents of CIE standard illuminants

Illuminant	Colour Temperature	Physical Equivalent
A	2856K	Tungsten filament lamp
B	4900K	Sunlight
C	6800K	Average daylight
D50	5000K	Daylight, UV-corrected
D55	5500K	Daylight, UV-corrected
D65	6500K	Daylight, UV-corrected
D75	7500K	Daylight, UV-corrected

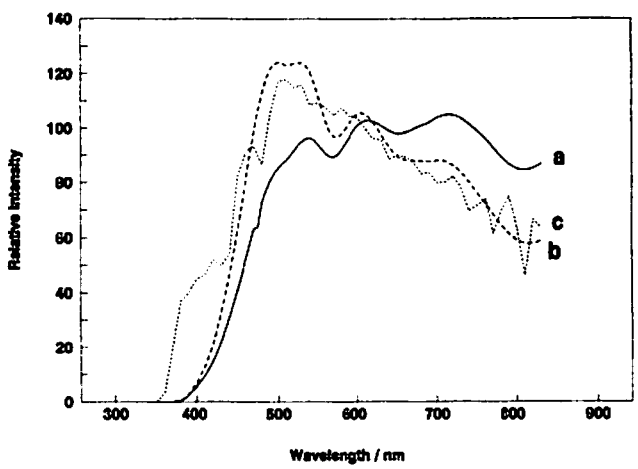

FIG. 1. Spectral power distributions of CIE Standard Illuminant (a) B, (b) C and (c) D_{65}.

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tendency for high errors, both between and within laboratories.

Attempts have also been made to quantify the colour of beer by reference to standard solutions of coloured liquids, including the set of three Brand dyes[4,5,20,21] and solutions of iodine[18], potassium dichromate[16] and aluminium iron (III) sulphate[9].

Spectrophotometric measurement now predominates as the method for assessing the colours of bright beers and worts, various correlations having been established for relating absorbance measurements at one or more wavelengths to the EBC scale[10]. Generally, methods relying on single wavelength measurements have used 430 nm. For instance, Nyborg and Trolle[19] made use of measurements at 430 nm and 530 nm. Brandon[6] proposed using the ratio of absorbances at 460 nm and 560 nm, whilst Stone and Miller[24] suggested also using a 700 nm measurement, to correct for turbidity. More recently, Baker[1] has described an instrumental analysis for beer colour using absorbance at 540 nm and this was formerly recommended by the IOB Analysis Committee[13]. Because of the similarity of their absorbance spectra to that of beer, solutions of potassium dichromate[22,23], Brand dyes[20,21], iodine solutions[18] and Hartong solutions (aqueous mixtures of potassium dichromate and sodium nitroprusside)[3] have all been proposed as calibration standards for spectrophotometers.

The EBC scale has, in the past, been generally regarded as being deficient in several respects for the analysis of beer colour. However, much of the evidence to date has been inconclusive, contradictory, or open to misinterpretation, thus lending weight to the argument for a re-assessment of beer colour measurement.

Tristimulus Measurement

Tristimulus measurement is an attempt to represent the colour of transmitted or reflected light, as individual intensities of red, green and blue. These quantities are given the symbols X (red), Y (Green) and Z (blue) and are specific to a chosen Standard Illuminant. For liquids, the values are also specific to the path length through which the object is viewed. Intensities are normally expressed in the range 0 (minimum intensity) to 1000 (maximum intensity). The lower the values, the darker the perceived colour. White light corresponds to 1000 units of X, 1000 units of Y and 1000 units of Z. Likewise, black corresponds to 0 units of X, Y and Z.

Tristimulus values can be obtained by applying three standard colour matching functions (Figure 2)[7] to transmission measurements made at wavelength intervals of 1 nm, 5 nm, 10 nm or 20 nm, across the visible range of the spectrum, in the manner described by Hunt[12]. The colour matching functions, defined according to CIE standards, have some physical basis, in that they correspond approximately to the light sensitivity of the three photosensitive pigments in the retina of the eye.

Variation in illuminating power across the spectrum is eliminated in spectrophotometric measurements by referencing measurements to air, water or some other suitable material. In this case, the transmission spectrum can, and indeed should, then be biased towards a particular colour temperature, by applying a weighting function or spectral power function for a standard illuminant, as defined by CIE.

Such methods have been applied to the determination of beer colour[19,25]. However, this is very time-consuming because of the many measurements needed to obtain accurate values. Some commercial instruments implement a version of this technique by making use of multiple filters arranged on a wheel attached to a stepper motor, so that multiple transmission measurements may be made automatically.

Simpler and more direct methods for obtaining tristimulus values have been tried, in which the transmitted light is split into red, green and blue components using filters, prisms or gratings. In this instance, the light source may be filtered or,

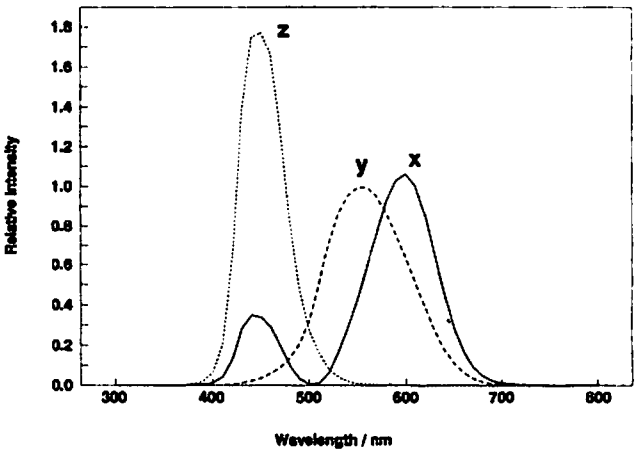

FIG. 2. CIE colour matching functions, Standard 2° Observer.

in some other way, adjusted so that its colour temperature matches some reference standard. In the first example of the application of tristimulus measurement to beers, Hartong and van den Hoek[11] described the derivation of tristimulus measurements by direct light intensity measurement, using three blue, green and amber filters whose transmission bands corresponded approximately to the three standard CIE colour matching functions. This principle has been improved upon recently, by one instrument manufacturer who has produced special 'tristimulus filters' which have transmission profiles very carefully matched to the standard CIE colour matching functions. In other instruments transmitted light is split into three broad spectral band widths, using gratings or prisms to allow approximate tristimulus values to be obtained directly.

Chromaticity Values

Various parameters may be derived from tristimulus values. One or other of these derived parameters may be chosen in preference to tristimulus values, because they may express the colour characteristics of a sample in a more convenient or meaningful form for a given application. One such set of parameters are chromaticity units, which represent the proportion of a particular colour in light transmitted through, or reflected by, the sample, ie:

$$x = \frac{X}{X+Y+Z} \quad y = \frac{Y}{X+Y+Z} \quad z = \frac{Z}{X+Y+Z}$$

where x, y and z are the chromaticity values of red, green and blue light in the sample respectively, with values of 0 (colour absent) to 1 (pure red, green or blue). White, or a neutral grey, theoretically corresponds to x, y or z, each having values of 0.333, except that the precise values will vary depending on the type of illuminant.

A set of chromaticity data was established for the Lovibond discs (corrected for Standard Illumination B) by Bishop[3] in 1966 (Figure 1a). These were based on accurate measurements by the National Physical Laboratory. Relatively recently, the illuminant used for the Lovibond discs, produced by the Tintometer Company, has been changed to Standard Illuminant C (Figure 1b). Some laboratory instruments also use Standard Illuminant D_{65} (Figure 1c):

Chromaticity values only give information regarding the proportions of a given colour in the sample and do not give an indication of the intensity of the colour. For instance, a colour which was comprised solely of red (x = 1.000) could appear as an intense colour (X = 1000), or as a dark tint (X = 0). In order to discriminate between these types of cases, the Y tristimulus value is usually used as a measure of the total light intensity received by the observer's eye, known as the luminance of the colour. Using this system, then, a colour

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is completely defined using the Y tristimulus value and any two of the three chromaticity parameters, x, y and z.

Conversion of Tristimulus Values to Other Derived Parameters

Other derived parameter sets include the CIE L*u*v*, Hunter LAB, LCH and CIE L*a*b* scales. The latter system is becoming more widely accepted, as something of a standard nomenclature for colour work, in a number of industries.

Values for L*, a* and b* are obtained from tristimulus values by the following relationships:

$$L^* = 116.(Y/Y_N)^{1/3} - 16$$

$$a^* = 500[(X/X_N)^{1/3} - (Y/Y_N)^{1/3}]$$

$$b^* = 200[(Y/Y_N)^{1/3} - (Z/Z_N)^{1/3}]$$

where X_N, Y_N and Z_N are the tristimulus values of a reference white, viewed under the standard conditions using the selected CIE Standard Illuminant. For CIE Standard Illuminant C:

$$X_N = 980.5$$

$$Y_N = 1000.0$$

$$Z_N = 1181.0$$

Materials and Methods

Canned and bottled commercial beers, representing a wide variety of beer types were obtained from retail outlets in the UK. All samples were degassed before analysis, by filtering through Whatman 91 general purpose filter papers. Samples of specialist malt extracts were obtained from Hugh Baird & Sons (Witham, Essex), Pure Malt Products Ltd (Haddington, East Lothian) and Munton & Fison (Stowmarket, Suffolk). "Colouring beers" and malt extract powder were obtained from Meyer-Bass (London) Ltd (London).

EBC colours were measured on beers according to the EBC Recommended Method[10], whereby absorbance of light is measured at 430 nm in a 1 cm glass or quartz cuvette, against water as the reference. The absorbance value is then multiplied by an empirically derived factor of 25, to give a colour value in terms of EBC colour units:

$$EBC = A_{430} \times 25$$

Transmission measurements were made using a Philips PU8720 UV/VIS scanning spectrophotometer in 1 cm cells, against distilled water as the reference. Transmission data were collected at 10 nm intervals in the region 350 nm to 800 nm.

Calculation of Tristimulus Values

At each wavelength of interest, the following parameters were calculated:

$$S_y = P.\bar{y} \quad (1a)$$

$$X/K = P.\bar{x}.(T/100) \quad (1b)$$

$$Y/K = P.\bar{y}.(T/100) \quad (1c)$$

$$Z/K = P.\bar{z}(T/100) \quad (1d)$$

where P is the value of the spectral power distribution of the selected standard illuminant at that wavelength; $\bar{x}$, $\bar{y}$ and $\bar{z}$ are the values of the red, green and blue CIE colour matching functions respectively, at that wavelength; T is the transmission of the sample at that wavelength.

The three tristimulus values were then calculated using the following:

$$X = [1000/\Sigma S_y].\Sigma(X/K) \quad (2a)$$

$$Y = [1000/\Sigma S_y].\Sigma(Y/K) \quad (2b)$$

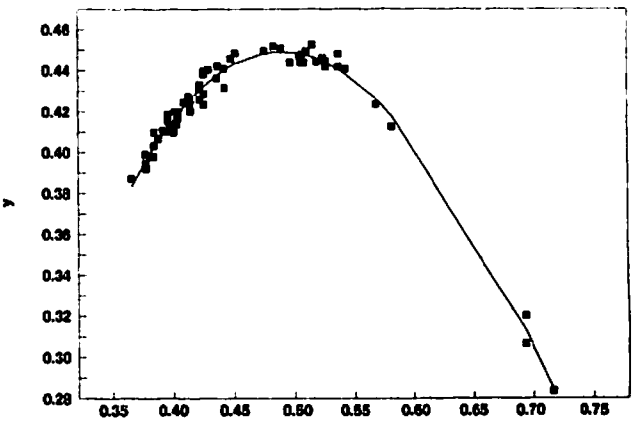

FIG. 3. Chromaticity values of commercial beers.

$$Z = [1000/\Sigma S_y].\Sigma(Z/K) \quad (2c)$$

where S_y, X/K, Y/K and Z/K are summed over the wavelength range 350 nm to 780 nm.

The colour matching functions used were those defined for the CIE 1931 Standard 2° Observer, over the range 380 nm to 780 nm, as published previously[7,8]. Values outside this wavelength range were assumed to be zero. The spectral power distributions for CIE Standard Illuminants, used in the calculations, were also as published by CIE[7,8].

Data processing was performed on an IBM XT-compatible computer, using proprietary spreadsheet software (Lotus 1-2-3 Version 2.2, Lotus Development Corporation, Cambridge, MA, USA). Additional programs were written using Turbo Pascal 4.0 (Borland International).

Results and Discussion

Tristimulus and Chromaticity Analysis of Commercial Beers

The transmission spectra of a wide variety of commercial beers were obtained, using a path length of 2.5 cm. The EBC colours of the beers were also determined. The tristimulus and chromaticity values of the beers were calculated and the x and y chromaticity values were plotted in the xy chromaticity colour space (Figure 3). The Y tristimulus value was plotted as a function of the EBC colour (Figure 4).

The chromaticity data (Figure 3) could be fitted by the following third-order polynomial:

$$y = 3.248x^3 - 8.691x^2 + 6.168x - 0.869$$

Ideally, this regressed curve should pass through the achro-

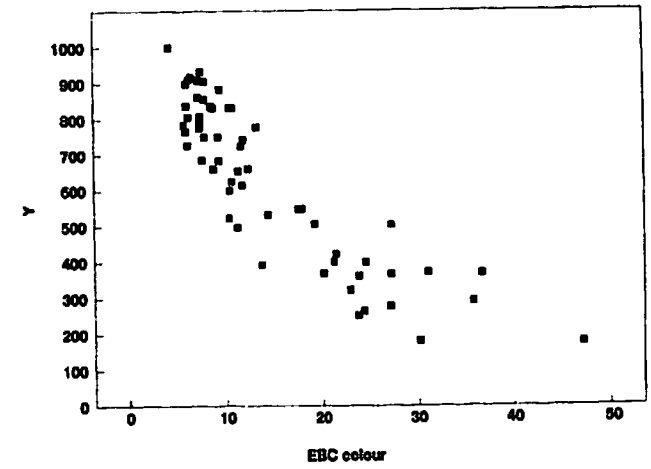

FIG. 4. Y tristimulus values of commercial beers.

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matic stimulus, N. This is the coordinate in the chromaticity colour space, which represents the point of neutral colour, ie. the point at which the proportions of red, green and blue are such that it appears as a neutral grey. The coordinates of this point will vary, depending upon which Standard Illuminant is being used. The representation of the achromatic stimulus, in terms of beer colour, is that of a material with an EBC colour of zero, ie. water. For Illuminant C, this point is represented by the point with the coordinates:

$$x = 0.3104 \qquad y = 0.3163$$

In practice, because of the clustering of data in only one region of the colour space, the regressed equation did not pass exactly through this point.

The regression of the chromaticity points (Figure 3) had a general form similar to the locus of xy chromaticity data for EBC colour scale (Figure 1a). Beers whose chromaticity values fall at the left hand of the regression curve (low x, low y), have correspondingly low EBC colour values. The maximum of the curve correlates to beers with EBC values of between 20 and 30 units. Beers and other materials with higher EBC values have chromaticity coordinates which fall on the right hand leg of the curve (high x, low y). Darker beers, therefore, have an increasingly dominant red component, x. The proportion of the green component, y, is at a maximum at approximately 25 EBC. The blue component, z, makes up a very small proportion of the total colour and is negligible for darker beers.

Generally, as would be expected, the calculated Y tristimulus values for beers (Figure 4) decreased with increasing EBC colour, as determined by the EBC Recommended Method. However, the scatter of points was too wide to make a statistical correlation meaningful. Given the wide spread of data points, it is difficult to see how the Y tristimulus value could be used as part of a colour measurement scheme for beers.

The Effect of Dilution on Beer Colour

The EBC scale is only defined explicitly up to a colour of 27 units, yet many beer types have colours which are quoted well in excess of this value. Strongly coloured materials, such as caramels and coloured malt extracts, have EBC colours of 2000 or more.

These higher colours are obtained either by diluting the sample, until it gives an EBC value between 20 and 27 (in the case of the method for the visual assessment of the colour of laboratory worts[14]), or by diluting until absorbance of less than 0.8, (ie. 20 EBC) is recorded (in the case of the method for bright beers[10]). In each case, the figure thus obtained is then multiplied by the appropriate dilution factor.

It is well known that changes in the dilution of a coloured liquid, or correspondingly, the sample path length, affect not only the intensity of the colour being measured, but also the proportions of red, green and blue, that make up the colour. To demonstrate this, a beer of approximately 60 EBC was progressively diluted with distilled water and the transmission spectrum was recorded at each stage, in a 2.5 cm cell. Tristimulus and chromaticity values were then calculated from these transmission data. Figure 5 shows these data plotted into the xy chromaticity space, in relation to the third-order regression obtained previously (Figure 3). The chromaticity values of the various dilutions follow a smooth curve. However, this curve only corresponds closely to the locus representing the best fit correlation at its extremes, where the EBC colours are approximately 6 EBC and 60 EBC respectively. Over the central portions of the two curves, especially in the region of 15 to 35 EBC, there is considerable deviation. The implication of this is that the diluted beer, with chromaticity values in this region of the colour space, will have a markedly different colour to the standard EBC colour. This will be particularly significant where visual comparison is being used for the assessment of beer colour.

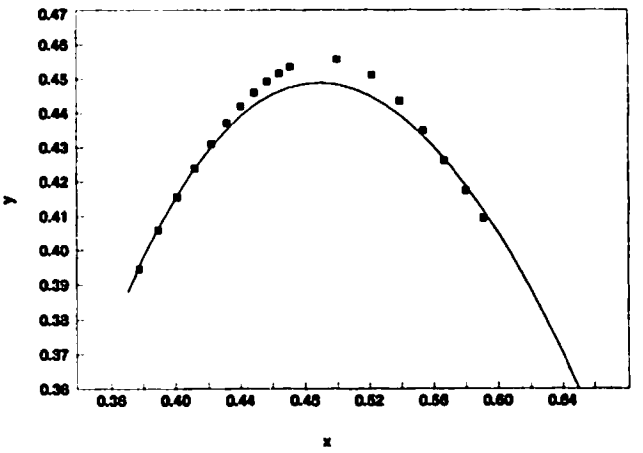

Fig. 5. Chromaticity values of a serially diluted beer (□) in relation to an experimentally derived regression for commercial beers.

The effect of dilution on tristimulus and chromaticity was further investigated by diluting a range of commercial beers to give the same absorbance at 430 nm (ie. the same EBC colour). The absorbance of the palest beer was measured at 430 nm, in a 1 cm cell, in accordance with the EBC Recommended Method. The remaining beers were diluted, such that they each had the same absorbance at 430 nm as the undiluted beer. The transmission spectra of all the beers were then recorded (Figure 6) in 2.5 cm cells. The tristimulus and chromaticity values for each beer were calculated from this transmission data. The x and y chromaticity coordinates of the beers were then plotted, in relation to the chromaticity coordinates of the EBC colour scale, in the region of 5.5 to 6.5 units (Figure 7). The reference beer, nominally of 6.2 EBC units of colour, which was not diluted for this experiment, had chromaticity values which indicated an EBC colour closer to 5.9 than to 6.2.

Despite the fact that all of the beers under investigation would have returned the same EBC colour, according to the Recommended Method, the chromaticity data show that each of the beers has a distinctly different colour, manifested by differing proportions of red, green and blue.

Colour Analysis of Colouring Agents

The colour characteristics of a range of colouring agents were also investigated. Caramels and malt extract pastes were diluted with distilled water. Malt extract powders were prepared by dissolving a suitable amount in distilled water.

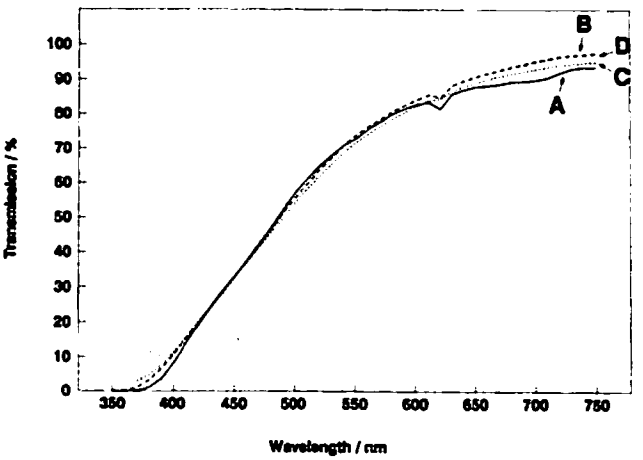

Fig. 6. Transmission spectra of four commercial beers (A, B, C and D) diluted to the same EBC value, using a path length of 2.5 cm.

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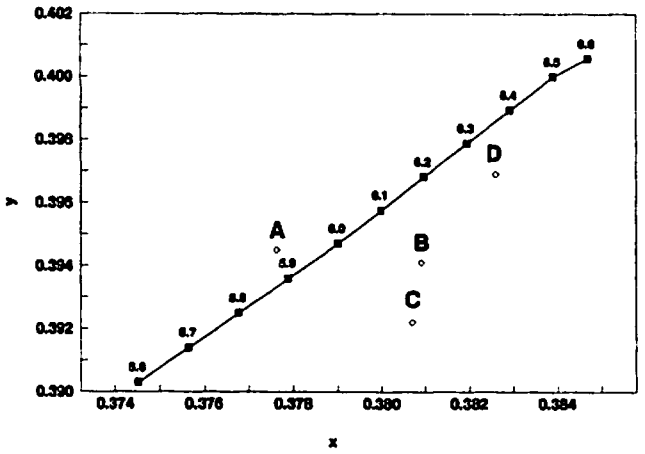

FIG. 7. Chromaticity values of four beers (A, B, C and D) diluted to the same EBC value, in relation to defined chromaticity values for the EBC scale.

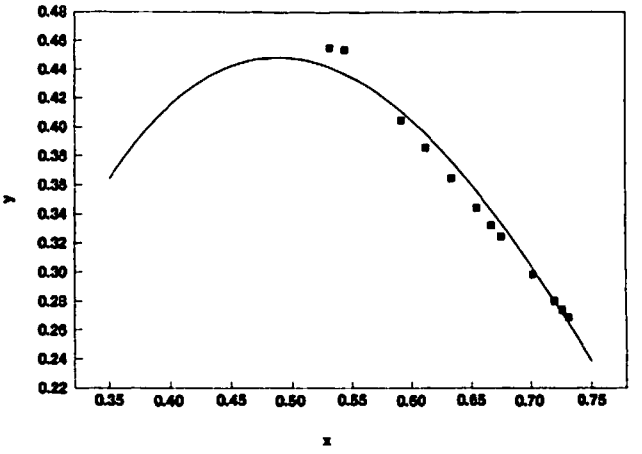

FIG. 9. Chromaticity values of colouring agents in relation to a regression of chromaticity values of commercial beers.

"Colouring beers" (ie. Farbebiers) were analysed without further dilution. The chromaticity and tristimulus values of the samples were obtained from their transmission spectra (2.5 cm path length), as described previously. The x and y chromaticity values for each material (diluted where necessary) were then plotted into the xy chromaticity space, as shown in Figure 8.

The points fitted a straight line regression of:

$$y = -0.96187\,x + 0.973067$$

The chromaticity values of these colouring agents were also plotted in relation to the "best fit" locus obtained previously (Figure 9). As in previous experiments, closer agreement was found with the EBC correlation at higher x values (and, correspondingly, higher EBC values), whereas significant variation was encountered in the mid-region of the correlation, corresponding to colours of approximately 25 EBC units.

Chromaticity Analysis of Mixtures

For chromaticity and tristimulus analysis of the colour of beer to be of benefit, it must provide information on the control of colour by the addition of colouring agents. For a mixture of two coloured materials with equal luminances, the following equations[12] describe the x and y chromaticity values of that mixture:

$$x = \frac{(m_2x_2/y_1) + (m_2x_2/y_2)}{(m_1y_1) + (m_2/y_2)} \qquad (3a)$$

$$y = \frac{(m_1y_1/y_1) + (m_2y_2/y_2)}{(m_1/y_1) + (m_2/y_2)} \qquad (3b)$$

where m_i is the number of luminance units of component i (ie. the proportion of component i in the mixture); and x_i and y_i are the x and y chromaticity values respectively of component i.

These relationships express what is known as the Centre of Gravity Law of Colour Mixture.

To investigate the validity of this relationship for beers, two commercial products, a pale lager and a stout, were mixed in varying proportions and the tristimulus and chromaticity values of each mixture obtained from the individual transmission spectra, measured at a path length of 2.5 cm (Figure 10). These x and y chromaticity values were then plotted into the xy chromaticity space (Figure 11), alongside the correlation previously obtained (Figure 3).

Also, equations 3a and 3b were applied to the set of chromaticity data for the co-dilutions of the two original beers, in order to determine theoretical chromaticity coordinates for the mixtures of the two beers. The locus of these calculated points was also plotted (Figure 11).

As with the serial dilution of a single beer, good agreement was only found between the chromaticity values of the mixtures and the EBC correlation at the extremes of the EBC scale, where one beer or the other was the major component of the mixture. At intermediate compositions, the chromaticity values of the mixtures exhibited significant deviation

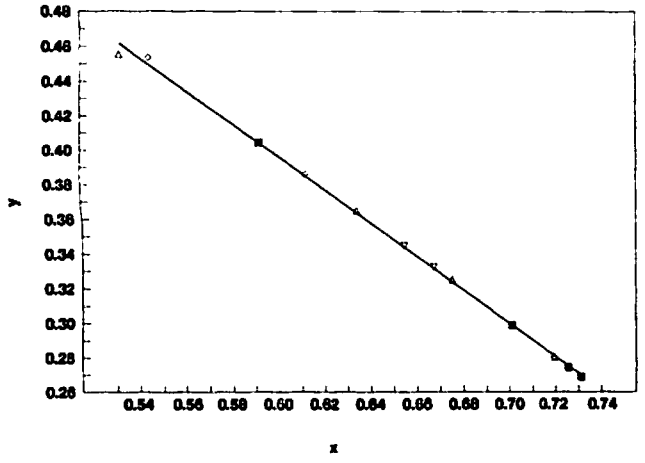

FIG. 8. Chromaticity values of colouring beers (□), caramels (◇), malt extracts (△) and malt powders (▽).

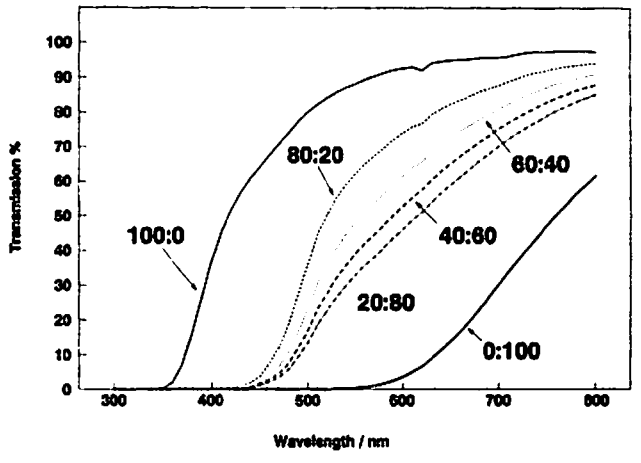

FIG. 10. Transmission spectra of mixtures of a pale beer (A) and a dark beer (B), in varying proportions (A:B, %v/v), using a path length of 2.5 cm.

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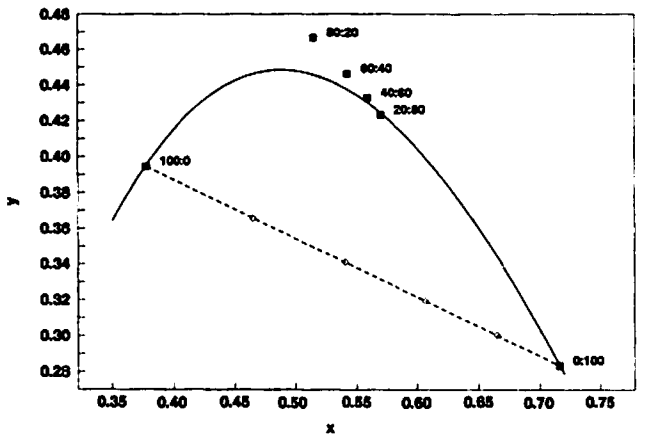

FIG. 11. Chromaticity values of mixtures of a pale beer (A) and a dark beer (B), in varying proportions (A:B, %v/v), in relation to an experimentally derived regression for commercial beers.

from the EBC correlation, indicating a 'non-standard' EBC colour.

The locus of predicted x and y chromaticity values for the mixtures was, as expected, a straight line between the two points, representing the original beers. The disparity between the experimental and theoretical chromaticity values for the set of beer mixtures is attributed to the fact that the luminances of the two beers, represented by the Y tristimulus values, differ substantially. Under these conditions, equations 3a and 3b do not hold.

Colour Control of Beer using Colouring Agents

In practice, for the accurate control of the colour of a given beer, the chromaticity values of the beer, the finished product, and any one of several available colouring agents, must be known. The remaining problems are, firstly, to select the most appropriate colouring agent to effect control and, secondly, to determine the required dosing rate.

Since mixtures of beers and similar materials do not obey the simple Law of Centre of Gravity of Colour Mixtures, selection of colouring agent and calculation of dosing rate is complicated.

Some illustrative calculations were performed on the effect of adding various amounts of different colouring materials to a commerical lager.

In an n component mixture and in accordance with Lambert's law:

$$A_{\lambda,i} = x_i[\log(1/T_{\lambda,i})] \quad (4)$$

where $T_{\lambda,i}$ is the transmission of component $_i$ at wavelength $_\lambda$; x_i is the proportion of component $_i$ in the mixture, by volume; $A_{\lambda,i}$ is the absorbance component $_i$ at wavelength $_\lambda$.

Summing for all n components, the transmission of the mixture at wavelength $_\lambda$, T_λ, is given by:

$$T_\lambda = \Sigma(1/10^{A_{\lambda,i}})] \quad (5)$$

Hence, the chromaticity values of a mixture can be determined, even where the luminances of the individual components vary greatly.

Using the above scheme, the chromaticity values were calculated for a commercial beer (approximately 11 EBC), with additions of colouring agents at a sufficient concentration to induce small colour changes in the original beer. The chromaticity values of the commercial beer were close to, but not coincident with, the EBC correlation determined previously. The loci representing the chromaticity values of the beer, with varying amounts of each of the colour agents added, were plotted in the xy chromaticity space, along with the "best fit" locus obtained previously (Figure 12).

Although chromaticity values of all of the colouring agents individually fall on the locus representing the EBC correlation, mixtures of the commercial beer with each of the colouring agents produce markedly different effects. Generally,the higher the proportion of red in the colouring agent, the greater the shift in beer colour, from the "best fit" locus to a colour with an abnormally high proportion of red. The addition of caramel, particularly, produced a substantial change in the colour of the beer, whereas this effect was less pronounced with malt-derived products. Both the samples of colouring beer and crystal malt produced colour shifts, which were in line with the "best fit" locus and, therefore, gave acceptable beer colours.

Mathematical Modelling of Transmission Spectra

For accurate tristimulus measurement of a sample, transmission values must be known throughout the visible region of the spectrum at intervals of at least 20 nm and, preferably, 10 nm or 5 nm. However, if tristimulus measurement is to become more widely accepted in the brewing industry as a method of determining the colour of beer, it would be a distinct advantage if the amount of data required for the calculation could be reduced. Consequently, a method was sought whereby a transmission spectrum of a beer could be modelled by a suitable interpolation technique from just a small number of transmission measurements. Transmission spectra of beers were thought to be particularly amenable to this technique, because of their smooth sigmoidal nature and the lack of any sharp absorbance bands.

Theoretical studies were carried out on a set of transmission spectra, obtained using a sample cell with a path length of 1.0 cm, for a range of commercial beers whose EBC colours ranged from 6.2 to 166.5 units. These beer types comprised lagers, a bitter, a strong ale and a stout.

A number of wavelengths, p_1 to p_N, in the region 350 nm to 800 nm, were chosen arbitrarily. For each transmission spectrum, a reduced set of data was created, comprising wavelengths, p_i, and transmittance values, q_i, at these selected points.

Curvilinear interpolation was then applied to the points in these individual reduced data sets, using Lagrange's classic formula for curvilinear interpolation, in order to calculate 'predicted' transmittance values, Q(p), at intermediate wavelengths between 350 nm and 800 nm:

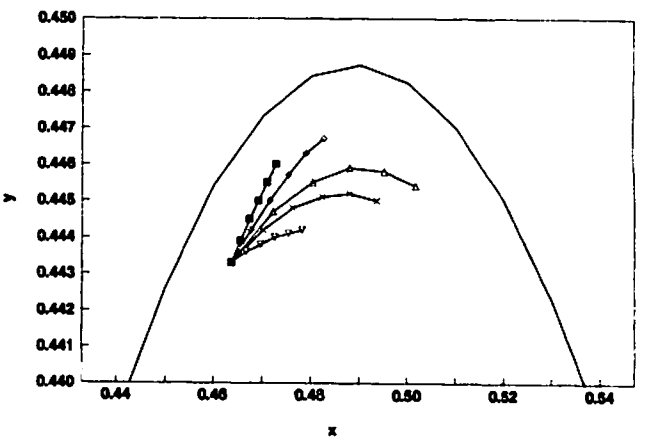

FIG. 12. The effect of the addition of colouring beer (□), crystal malt extract (◇), roasted barley extract (△), chocolate malt extract (X) and caramel (▽) on the chromaticity values of a beer. The values are plotted in relation to an experimentally derived regression for commercial beers.

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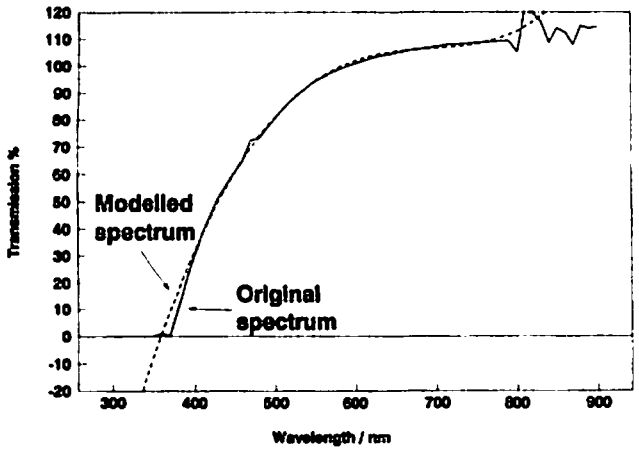

FIG. 13. Comparison between an experimentally obtained transmission spectrum of a beer and an interpolated spectrum using transmission measurements at 360 nm, 450 nm, 540 nm, 670 nm and 760 nm, using a path length of 1 cm.

$$Q(p) = \frac{(p-p_2)(p-p_3)\cdots(p-p_N)}{(p_1-p_2)(p_1-p_3)\cdots(p_1-p_N)}\,q_1 + \frac{(p-p_1)(p-p_3)\cdots(p-p_N)}{(p_2-p_1)(p_2-p_3)\cdots(p_2-p_N)}\,q_2 + \frac{(p-p_1)(p-p_2)\cdots(p-p_{N-1})}{(p_N-p_1)(p_N-p_2)\cdots(p_N-p_{N-1})}\,q_N \qquad (6)$$

where Q(p) is the predicted transmission at intermediate wavelength p, and p_i are the wavelength and transmission respectively of the $_i$th point and q_i in the reduced data set of N chosen points.

The Lagrange formula produces a polynomial curve of order (N−1), which passes through each of the N reference points, but which may deviate quite widely at intermediate points. In this study, the selection of the correct reference points was the key to minimising large oscillations of the interpolated curve.

For each beer, the degree of fit, between the interpolated spectrum and the original spectrum, was assessed by calculating the sum of the squares of the differences (SSD) between the transmission values of the interpolated and the original spectra, at 10 nm intervals between 350 nm and 800 nm. An example of a fully optimized system, using five set points, is shown in Figure 13.

This process was repeated, using different sets of selected wavelengths, until the mean of the SSD values for all of the beers was minimized. The resulting set of wavelengths represented an optimized system, which gave the best set of predicted spectra for the range of beer colours studied.

This procedure was used to identify optimized systems comprising 3, 4, 5, 6 and 7 selected wavelengths between 350 nm and 800 nm. The optimized wavelengths for each system are collated in Table II and the SSD values for the spectra of each beer, in each system, are presented in Table III.

TABLE II. Optimized wavelengths for the modelling of transmission spectra of beer using Lagrange interpolation

No of Points	Wavelengths/nm						
	1	2	3	4	5	6	7
3	390	550	730	—	—	—	—
4	400	450	640	750	—	—	—
5	360	450	540	670	760	—	—
6	360	400	450	540	670	760	—
7	360	400	450	540	670	760	780

TABLE III. Sums of the squares of the differences (SSD) between experimental and interpolated transmission spectra for a range of commercial beers

Beer	EBC Colour	Number of points in the interpolation				
		3	4	5	6	7
A	6.2	1447.9	219.0	149.4	176.4	170.8
B	10.5	407.8	160.5	61.9	34.3	32.7
C	23.0	1091.4	441.5	43.5	102.8	16.5
D	50.8	2637.1	579.0	187.2	257.2	17.7
E	166.5	324.8	149.6	56.3	13.8	15.4
Mean		1181.8	309.9	99.7	116.9	50.6

Tristimulus and chromaticity value were calculated for each beer, firstly using the original transmission spectrum and, secondly, using the modelled transmission spectrum. In each case, transmission values obtained, using a sample cell with a 1 cm path length, were first normalised to a path length of 2.5 cm by applying the Beer-Lambert Law (equations 4 and 5). A comparison of the two sets of results is given in Table IV.

Differences between the two sets of results, for a given beer within the chromaticity colour space, ΔE, were assessed according to the relationship:

$$\Delta E = \sqrt{(x_1-x_2)^2 + (y_1-y_2)^2}$$

where x and y are chromaticity values and $_{1\ 2}$ represent the original and modelled spectra, respectively.

Even though all wavelength points were allowed to vary during the optimization procedure, it is interesting to note that the same optimized wavelengths recur in the 5-, 6- and 7-point models. It is likely that optimized models, containing more than seven points, would include the wavelengths of the optimized seven-point model as a subset.

Generally, the more reference points that were included in the model, the better was the fit between original and modelled spectra, although the improvement in fit between the 5- and 6-point systems was only small (Table III). The mean SSD value decreases very rapidly, as the number of points increases from three to four and from four to five, but the apparent improvement in fit between original and calculated spectra quickly becomes limiting.

The overall paleness or darkness of a beer did not necessarily give an indication that the transmission spectrum of the beer would be accurately modelled, according to SSD values (Table III). When considering the differences in calculated chromaticity values derived from the original spectra and the modelled spectra (Table IV), the accuracy of the chromaticity values appears to deteriorate as the beer colour increases. However, accuracy is still quite acceptable over all beer colours. The accuracy would be further improved by reducing the wavelength internal from 10 mm to 5 mm, or to 1 nm.

CONCLUSIONS

Commercial beers have been shown to possess a range of chromaticity values forming a locus in the xy chromaticity space, which may be thought of as the range of normally "acceptable" beer colours. This locus is similar to the locus of the standard EBC colours, as defined by the Lovibond discs. However, dilution of an intensely coloured beer, to permit the use of the EBC or IOB Recommended Method, results in samples with atypical colours and, therefore, they cannot be accurately represented by an EBC number. This

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TABLE IV. Comparison of tristimulus and chromaticity values for beers obtained from experimental and interpolated transmission spectra

Beer	EBC	Full Analysis			7-point Interpolation			
		x	y	Y	x	y	Y	ΔE
A	6.2	0.3776	0.3945	726.9	0.3874	0.3951	728.7	0.00100
B	10.5	0.4221	0.4258	599.2	0.4241	0.4254	606.2	0.00204
C	23.0	0.5050	0.4469	319.7	0.5077	0.4449	326.6	0.00336
D	50.8	0.7165	0.4125	148.9	0.5832	0.4104	149.7	0.00247
E	166.5	0.7165	0.2834	0.5	0.7076	0.2923	0.6	0.01259

is amply demonstrated by the fact that the dilution of a range of beers, to the same EBC value, results in liquids with demonstrably different chromaticity values. Under these conditions, visual comparison of the diluted beer, with a set of colour standards, will invariably result in large errors because the sample cannot be matched exactly.

Similar problems are encountered with beers which have had their colours adjusted using colouring agents. The extent of the problem depends on the colourant.

The adoption of tristimulus and chromaticity values, as the primary standard for the colour analysis of beer, is feasible because it relies only upon transmission measurements, which may be carried out in most laboratories. The technique may be applied to all beers, no matter how dark they are in colour, without dilution. In order to reduce the number of measurements that are required for the analysis of a sample, a simplified method based on transmission measurements at a limited number of wavelengths can be employed. This shorter method has only small errors for all beer types when compared with analysis employing transmission values over a full range of wavelengths.

A suitable, inexpensive and relatively rapid method for the determination of beer colour in terms of tristimulus or chromaticity units would, therefore, comprise the following steps. Firstly, transmission measurements are made at 360 nm, 450 nm, 540 nm, 670 nm and 760 nm on an undiluted beer in a cell with a path length of 2.5 cm. Alternatively, measurements may be made using a 1 cm path length and then normalised to 2.5 cm, by applying the Beer-Lambert Law (equations 4 and 5). Secondly, curvilinear interpolation is applied to these measurements in order to generate a set of calculated transmission values at 10 nm intervals, in the range 360 nm to 780 nm (equation 6). Finally, tristimulus values are calculated from this set of interpolated transmission values, using the CIE Colour Matching Functions for a secondary Observer and the spectral power distribution for the CIE Standard Illuminant C (equations 1 and 2). The resulting tristimulus values may then be converted to any desired subset of colour parameters, such as chromaticity, L*a*b*, etc.

The above data analysis process has been implemented in the form of an automated, macro-driven spreadsheet, designed to run with Lotus 1-2-3 Version 2.0 or later, or any other Lotus 1-2-3 compatible spreadsheet software, running under DOS on an IBM PC/XT/AT-compatible computer.

Acknowledgements. The author wishes to thank the Director of BRF International for permission to publish this paper.

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