Paper Microelement Composition and its Effect on Components of the Color Difference dE94 in the Paper Shade

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Abstract: - In the printing industry, whiteness and shade of paper significantly affect the final print. However, the term "whiteness" still does not have a precise definition. Different international standards define whiteness differently. The composition of the paper obviously affects whiteness, but little is known about the effect on whiteness that a particular chemical element produces in paper. Not all paper is recycled by industrial means, so some of the impurities from paper can penetrate into the soil and water. If these impurities are unsafe, this may create an additional threat to the environment and people. In this work, we have established a link between the whiteness of paper and its component composition. We compared 255 paper samples by their dE94 color difference versus standard paper with CIE Lab coordinates (95/0 / –2). X-ray fluorescence analysis revealed the presence of 25 chemical elements in paper samples. Based on this, clustering of papers and further discriminant analysis revealed four clusters with distinct composition and whiteness of paper. We identified 12 elements that have the greatest impact on the whiteness of paper (S, Ti, Mn, Zn, Rb, Sr, Y, Zr, Sb, I, Ba, Th), and also built a model of the influence of the composition of the paper on its whiteness, based on artificial neural networks.

Key-Words: - paper, whiteness, color difference, fillers, cluster, discrimination

1 Introduction

While one percepts the quality of the print production, the most important property of a paper is its whiteness [1,2]. Whiteness is a complex property of visual sensation, characterizing the degree of approximation of an object to white in strength of its brightness, high scattering ability and minimal color shade. It is known that the shade of printing paper appears solely as a result of production technology. In the literature it has been repeatedly shown that there is a stable interrelation between the printing and optical properties of paper. The influence of the mineral content on the whiteness of the paper is great [3], but manufacturers do not disclose information on the composition of fillers in paper and coating layers. The situation is complicated by the lack of control of the whiteness of paper on most of the printing industries. proceedings. Furthermore, it is hard to find studies on such a topic as most of paper found are related to the paper fillers and do not show their particular links with paper optical properties.

The parameter "whiteness" can be specified in accordance with two valid international standards by one of the methods differing in the dimensionality of the result. Integral (i.e. without taking into account spectral information) the whiteness (brightness) index is determined by the method according to ISO 2470-77 [4, 5]. It shows how light is diffusely reflected within the visible spectrum at an effective wavelength of 457 nm. Measurement of whiteness as a percentage of the standard by this method is performed using photometers. This method shows only how much more or less light in the visible region of the spectrum is able to reflect this sample in comparison with the standard, whilst the whiteness may exceed 100%. And, without specifying the standard, this information does not make sense. According to the method of the International Commission on Lighting (CIE), the diffuse energy brightness coefficient is measured in the full visible spectral range under illumination conditions from different light sources and different types of observer (ISO 11475, ISO 11476) [6, 7]. The method makes it possible to estimate the degree of whiteness of a sample containing optically brighteners and tinted dye elements. However, the method can only be used when standardized spectrophotometric equipment is used, which limits the scope of its application.

Thus, the whiteness of the CIE is calculated from the chromaticity coordinates and is expressed in conventional units, whilst the ISO brightness is expressed as a percentage and any deviation from 100% indicates a color shade, a direct comparison of whiteness by ISO and CIE is not possible; the quality of the printed matter must correspond to ISO 12647 – 2 [8], where the paper requirements are set, in particular CIE Lab coordinates for the main types of print paper (for example, for coated paper it is 95/0/–2), however, at present, there is no model for linking the mineral content in the fillers of paper and coating layers and the whiteness of paper.

In the literature, there were some attempts to link the paper fillers content with the paper properties. For instance, in the works [9, 10], the authors noted that dozen fillers used make it possible for the papermakers to meet customer requirements for opacity or brightness at lower net cost. However, brightness is not entirely inherent in the crystalline nature of a papermaking filler. Rather, it depends on particle size and the amount of pressure applied during the paper brightness measurement. At the same time, the papers did not offer any numerical link between the paper content and its brightness.

The main composition of printing paper varies little at different manufacturers and is known quite well. Paper consists of pulp ($[C_6H_{10}O_5]_n$ or $[C_6H_7O_2(OH)_3]_n$), traces of lignin, Ca^{2+}, Mg^{2+}, Na^+, NH^{4+} cations, remnants of a mixture of caustic soda and sodium sulfide ($NaOH + Na_2S$) during sulphate cooking, chlorine residues from bleaching, clay, titanium dioxide (TiO_2), calcium carbonate ($CaCO_3$), aluminum hydroxide ($Al(OH)_3$), talc ($Mg_3Si_4O_{10}(OH)$), calcium sulfate ($CaSO_4$), barium sulfate ($BaSO_4$), natural or synthetic silicates or silicate pigments and zinc pigments, as well as dyes and pigments (including optical brighteners). The average amount of mineral fillers in paper reaches 7.1%, while the total amount of carbonate fillers reaches 57% of their total amount [11].

Some manufacturers replace the more expensive raw cellulose in paper with cheaper mineral fillers. In the literature, a quantitative or qualitative comparison of various types of printing paper made with such technology features has not found, therefore, it is impossible to judge the validity of such a replacement. Also, no scientific papers linking the mineral composition of the paper composition and coating layers with the optical characteristics of the paper were found.

The desire of manufacturers to increase the whiteness of paper by adding to its composition a variety of substances instead of cellulose leads to an increase in the diversity of chemicals in paper. In this case, the degree of purity of the mineral fillers, which are used in the manufacture of paper and its coating layers, has a great influence on this diversity. The lack of accurate information about the content of certain mineral fillers in paper can pose a certain threat to the environment and people, since not all paper is recycled by industrial methods, and part of the paper waste is in contact with soil and water. Thus, the whiteness of paper indirectly affects the possible environmental effect of papermaking industry.

It is known that there is a miscommunication between papermaking and graphic arts industries. This particularly is reflected in the paper whiteness/brightness measurement. Pulp and paper at factories is assessed by its brightness (the diffusion reflection at 457 nm) while paper at printing plant and in graphic art as a whole is defined by the whiteness and the shade that are calculated by the well-known CIE formulas.

These are two completely different matters, though practitioners have to account them in order to obtain a precise result of print. The work [12] shows the way to achieve a communication between the industries by the help of precise spectrophotometric measurements and color difference assessment. Paper samples in the work are measured with white (self) backing. The significant issue indicated is the total inter-measurement tolerance while different devices are applied. Color difference dE might act as a quantitative measure of perceptual difference of paper whiteness. Moreover, the color difference dE assessment based on the spectrophotometric measurements is often used as a measure of the paper samples diversity [13]. There are a few color difference formulas, however, it is dE94 [14] that combines precision and relative simplicity for computations. The dE94 formula combines lightness (L), color tone-hue (H) and saturation (S) that represent color coordinates in cylindrical coordinate system.

In this work, we use CIE Lab coordinates 95/0/–2 as a whiteness standard for print paper (standard paper). Based on this standard, we compare whiteness of print paper samples using dE94 color difference formula. For clarity, the angle of the color tone was expanded into a linear axis. Thus, we can represent the results in a three-dimensional

Euclidean space. We, also, measure paper fillers contents and reveal the dependence of paper whiteness on the content. Based on it, we carry out the clustering of samples. Such, we establish the relationship between paper fillers contents and paper color coordinates (i.e. whiteness).

2 Approach and Experimental

For the experiment, 255 samples of coated print paper were selected. All samples were measured in the form of thick pile (100 sheets and more) by a spectrophotometer X-Rite iOne Pro. Thus, 255 spectra and CIE Lab coordinates were obtained. For each sample's CIE Lab coordinates, we calculated dE94 color difference by formula (1).

$$dE94 = \sqrt{\left(\frac{\Delta L}{k_L S_L}\right)^2 + \left(\frac{\Delta C_{ab}}{k_C S_C}\right)^2 + \left(\frac{\Delta H_{ab}}{k_H S_H}\right)^2}, \quad (1)$$

were

$\Delta L = L_1 - L_2,$

$\Delta C_{ab} = \sqrt{{a_1}^2 + {b_1}^2} - \sqrt{{a_2}^2 + {b_2}^2},$

$\Delta H_{ab} = \sqrt{(a_1 - a_2)^2 + (b_1 - b_2)^2 - (\Delta C_{ab})^2},$

$S_L = 1,\ S_C = 1 + K_1 C_1,\ S_H = K_1 C_1,$

$k_L = 1, K_1 = 0{,}045, K_2 = 0{,}015.$

Instead of using a hue difference ΔHab as it described above, we apply the direct angles difference (2):

$$\begin{gathered} \Delta h = h_2 - h_1 \\ h_2 = atan\frac{b_2}{a_2} \\ h_1 = atan\frac{b_1}{a_1} \\ h_1, h_2 \in [-180; 180] \end{gathered} . \quad (2)$$

Paper samples were also measured by X-ray fluorescence spectrometer INNOV X-5000 (XRFA). The device is intended for non-destructive analysis of the chemical composition of metals, powder, liquid samples etc. Several elements from phosphorus (P) to uranium (U) are simultaneously determined by measuring the spectrum of secondary X-ray radiation, which depends on the elemental composition of the sample. Thus, concentrations of 25 elements in each sample were obtained. In order to obtain the dependence of paper whiteness on paper composition, we reveal clusters in paper based on the components of color difference dE94: dL, dC, dH.

Then, we develop a discriminant analysis that divides papers by their elements content. Analysis were carried out in Statistica 10 package.

The establishment of the relationship between the microelement composition of paper and its whiteness was carried out with the involvement of machine learning apparatus. An artificial neural network (ANN) of the multilayer perceptron with one hidden layer was used (see Fig.1). It was prepared in the MABLAB environment. The framework selection was done by brute force algorithm: the number of neurons in the hidden layer vary from 1 to 20 units. The best performance was assessed by comparison of root mean squared errors (RMSE) (3).

$$MSE = \sqrt{\frac{\sum_{i=1}^{n}(y_{modeli} - y_{reali})^2}{n}} . \quad (3)$$

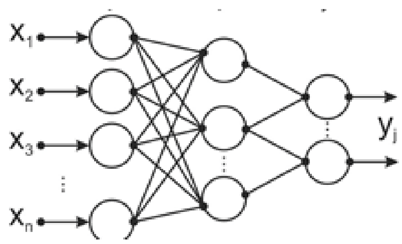

Fig. 1. Artificial neural network of multilayer perceptron.

The input data were concentrations of 12 determining chemical elements in the paper (12×255 matrix). The outputs were the color coordinates of the sample (2×255 matrix). To reduce the dimensionality of the output data and to increase the accuracy of prediction, the coordinates of the CIE Lab were converted into a binary from the chromatic (CIE C, root mean squared sum of chromatic coordinates of CIE a, b) and luminance (CIE L) components.

3 Results and Discussion

As indicated above, 255 print paper samples were selected and measured. The form of spectra are shown in Fig.2 and Fig.3 where the characteristic spectra of coated and uncoated paper as well as a bleached pulp spectrum are given.

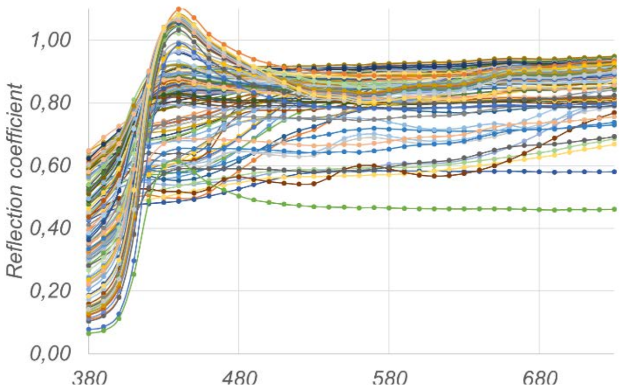

Fig. 2. Reflection spectra for the sample papers

It seems difficult to determine the characteristics among such a large number of samples. Therefore, it was decided to cluster the sample. As a criterion for clustering, the differences in lightness, saturation, and color tone between sample and standard paper were chosen. The clustering has been carried out in Statistica 10 package using the method of k-means. This procedure revealed four distinguishable clusters in paper samples (see Fig.4).

Next step was the search of interconnection between clusters and paper fillers contents based on data from XRFA analysis.

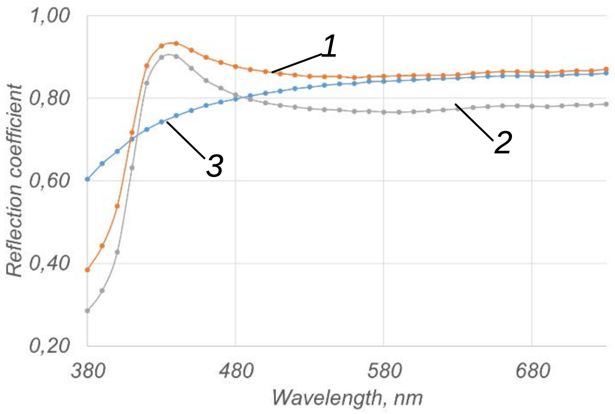

Fig. 3. The characteristic spectra for coated paper (1), uncoated paper (2) and bleached pulp (3)

The elements found during X-Ray fluorescent analysis: S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Y, Zr, Mo, Sb, I, Cs, Ba, Pt, Hg, Pb, Th. The concentrations of each element were highly dispersed and distributions were skewed. The descriptive statistics are shown in Table 1.

TABLE 1. DESCRIPTIV STATISTICS OF THE OBSERVED ELEMENTS

Element	Min concentrations, ppm	Max concentrations, ppm	Mean concentrations, ppm	MSE, ppm	Skewness
S	0	21988.00	3881.39	3352.63	1.45
Cl	0	83126.80	2481.83	5633.73	12.33
K	0	27369.00	1640.11	2729.90	4.74
Ca	0	943967	699462.17	554026.12	0.64
Ti	0	70872.00	2146.89	5444.65	9.76
Cr	0	243.00	23.65	24.18	4.41
Mn	2.67	958.00	96.92	84.63	5.84
Fe	96.30	10208.00	2218.26	1762.52	1.55
Ni	0	193.00	6.74	21.71	4.23
Cu	0	171.00	9.40	28.07	3.92
Zn	0	245.00	9.83	31.52	4.47
As	0	34.00	21.30	6.62	–1.73
Rb	0	66.00	5.55	5.00	2.72
Sr	0	2383.00	451.31	629.60	1.74
Y	0	838.00	539.87	209.70	–1.24
Zr	0	963.00	97.57	140.12	7.00
Mo	0	30.00	2.37	6.52	2.62
Sb	5.99	382.00	151.12	71.32	1.16
I	0	2518.40	272.69	649.70	2.24
Cs	0	5702.90	384.50	1195.72	2.99
Ba	0	578.00	119.81	91.12	1.43
Pt	0	123.00	34.13	36.23	0.40
Hg	0	91.50	1.88	7.20	8.28
Pb	0	31.00	2.09	5.81	2.72
Th	643	1440.00	1119.45	178.29	–0,93

In view of such an abnormal behavior of the elements distributions, we have to make a normalization procedure in order to be able to carry out the analysis. The normalization is based on logarithmic transformation and relation with Calcium (Ca) concentration as it has shown the maximum content among all elements. Thus, normalized concentration of ith element (x_{inorn}) accounts the initial concentration (x_i), concentration of Calcium (x_{Ca}) and is calculated by formula (4):

$$x_{inorn} = \log_{10} \frac{x_i + 1}{x_{Ca} + 1} . \quad (4)$$

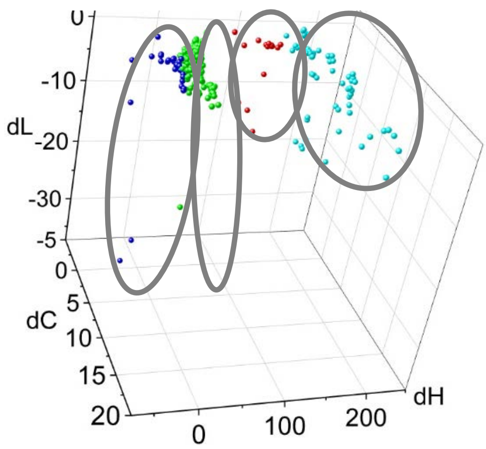

Fig. 4. Four revealed clusters based on color difference

Based on the clusters revealed, we carry out the discriminant analysis. Numbers of clusters introduced the a-prior probability. The final discrimination revealed that a-posterior classes are nearly completely coincided with clusters (see the classification matrix in Table 2). Total correct percent is 81.57 that is rather high value. Such, we may affirm that discrimination is almost coincides with clustering. Moreover, it confirms the almost identical division of the sample according to two independent criteria, color coordinates and chemical composition. Thus, a direct relationship between the composition of the paper and its whiteness has been established.

TABLE 2. CLASSIFICATION MATRIX OF DISCRIMINANT ANALYSIS

Group	% correct	G1, p=0.59	G2, p=0.55	G3, p=0.11	G4, p=0.28
G1-1	53.33	8	6	0	1
G2-2	87.14	6	122	2	10
G3-3	50.00	0	10	14	4
G4-4	88.89	0	8	0	64
Total	**81.57**	**14**	**146**	**16**	**79**

The analysis also revealed 12 elements that mostly affect the color shade of the paper: S, Ti, Mn, Zn, Rb, Sr, Y, Zr, Sb, I, Ba,Th. The Table 3 shows the discriminant function analysis summary accounting four grouping clusters. The most-effect elements are highlighted in bold.

Some of the elements (S, Cl, K, Ti, Ca, Zn, Ba) might be found in the paper composition as they are used in the production process. However, there are no ideas about the origin of such exotic elements as Rb, Sr, Y, Cs, Th, moreover, some of them radioactive. This is the issue that must be carefully studied.

Nevertheless, it can be assumed that it is the compounds of these chemical elements that form the substances responsible for the paper color shade.

TABLE I. DISCRIMINANT FUNCTION ANALYSIS SUMMARY

Element	F-remove (3,228)	p-value	Tolerance
S	4.867	0.003	0.514
Cl	1.000	0.394	0.408
K	0.724	0.538	0.470
Ti	11.840	0.000	0.369
Cr	1.058	0.368	0.334
Mn	15.976	0.000	0.188
Fe	1.938	0.124	0.209
Ni	0.255	0.858	0.097
Cu	0.779	0.507	0.062
Zn	8.041	0.000	0.048
As	2.476	0.062	0.277
Rb	4.779	0.003	0.384
Sr	8.360	0.000	0.302
Y	5.343	0.001	0.438
Zr	9.638	0.000	0.501
Mo	2.603	0.053	0.183
Sb	8.458	0.000	0.143
I	5.921	0.001	0.254
Cs	1.066	0.364	0.075
Ba	2.756	0.043	0.439
Pt	2.253	0.083	0.434
Hg	0.592	0.621	0.128
Pb	1.327	0.266	0.075
Th	4.253	0.006	0.093

To establish the relationship between paper microelements composition and its whiteness we have attracted the apparatus of machine learning. The artificial neural network of multilayer perceptron with one hidden layer was acted as an interpolator. The input data were paper chemical components concentrations, the output data were paper samples color coordinates. The learning algorithm of the famous Levenberg-Marquardt technique with the Bayesian regularization assumed at each training epoch a random partitioning of the input set into training and test samples and the absence of a validation sample, which increases the training and test samples. The training sample was used to train the network, and the results of the forecast were compared with the test sample data. As a criterion for prediction accuracy, the root-mean-square error was used.

Configurations of the ANN were represented by a set of 20 networks with one hidden layer and a different, from 1 to 20 number of neurons in the hidden layer. Determination of the best network configuration was performed by iterating cycles from 30-fold training of each of the configurations of the INS and determining the standard deviation in each case. The network configuration with 2 neurons in the hidden layer provided RMSE with an average value of 0.179; network configuration with 3 neurons reached 0.134. Thus, ANN with 3 neurons in the steep layer showed an advantage in the accuracy of the prediction.

To check the stability of the prediction result, another computational experiment was conducted, consisting of 100 ANN training sessions with three neurons in a hidden layer. The average value of the standard deviation of the experiment was 0.123. Thus, the INS has demonstrated a high prediction accuracy and the possibility of using this method to predict the whiteness of a paper sample according to its elemental composition, which is convenient for both the printing and papermaking industries.

4 Conclusion

Until now, the relationship between the content of chemical elements in paper and its whiteness has not been established. It was argued that the paper parameters depend on its composition, but no quantitative estimates have been found in the literature, as well as a universal method for paper whiteness assessment.

Since the term whiteness itself is not completely operational and depends on both the context of application and the industry, we decided to use the parameters from ISO 12647-2, namely the paper's color coordinates (CIE Lab 95/0/–2), as a criterion of the whiteness of the paper.

As a quantitative estimate of the difference in whiteness of paper samples and the standard, a color difference formula dE94 was used. The components (variables) from this formula also acted as a convenient basis for the visualization of results. In particular, we turned the cylindrical component of the color tone to the linear axis, which made it possible to obtain the figure 3. The use of such a basis also allowed to cluster samples and identify 4 clusters with a clear difference in color.

In samples of paper, 25 chemical elements heavier than Phosphorus were detected. The abnormal distribution of the concentrations of these elements made further analysis impossible. We suggested using concentration values normalized to calcium, since calcium is the maximum concentration in all samples.

On the basis of the detected clusters, a discriminant analysis was carried out according to the paper composition criterion. The analysis with a probability of 82% confirmed that the separation into clusters is carried out not only by the color coordinates, but also by the chemical composition, which directly proves the interconnection between the shade of paper and the exfoliation of its fillers.

12 elements that most affect the shade of paper: S, Ti, Mn, Zn, Rb, Sr, Y, Zr, Sb, I, Ba, Th. Some of the detected elements of papermaking technology cannot be detected in it, but they are detected. This means that undesirable impurities that penetrate into the composition of the paper during its manufacture, can significantly affect the shade of the resulting material. In addition, the presence of elements that are especially dangerous for the environment and human health, such as rubidium, strontium, barium, thorium, raises issues of recycling paper in a new light. Therefore, these issues must be strictly controlled.

A computational experiment on the selection of a neural network and its use to predict the whiteness of paper based on its mineral composition has shown broad prospects for further improvement of this method. As data on the composition and content of mineral components in paper are refined, it is possible to modify the input data for ANN.

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