SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
11 (2005)

CONDITIONS OF PREPARATION AND THEIR INFLUENCE ON RESULTING PIGMENT COLOURS

Milan JAVŮREK[a1], Petra ŠULCOVÁ[b] and Miroslav TROJAN[b]
[a]Department of Process Control and Computer Techniques,
[b]Department of Inorganic Technology,The University of Pardubice,
CZ–532 10 Pardubice

Received September 29, 2005

Inorganic mixture pigments are prepared by reaction in solid phase at various temperatures of calcination. We tested trichromatic coordinates of these products vs. temperature. These curves are deformed. Data was analysed by ANOVA statistical method and show that reaction conditions are in interaction. The interaction may be smaller by addition of crystallization agents or another change of reaction conditions.

Introduction

Colour properties are described in terms of CIE $L^*a^*b^*$ (1976), values L^* represent the lightness or darkness and values a^* (the green – red axis) and b^* (the blue-yellow axis) indicate the colour hue (Ref. [1]).

Trends of colour values a^* and b^* are studied during evaluation of pigment

[1] To whom correspondence should be addressed.

colours considering dependence on conditions of their preparation. The aim is to optimise conditions of the pigment preparation (temperature, composition) with regard to desired colours. However, the dependences indicate special anomalies and can change into completely degraded dependences without any unambiguous trend (Fig. 1). For this reason, primary data were submitted to a statistical analysis to find out systematic error in the pigment assessment. The method of variance analysis (ANOVA, Ref. [2]) was used for data evaluation to examine the precision of data and influence of individual conditions of pigment preparation to the resultant colour.

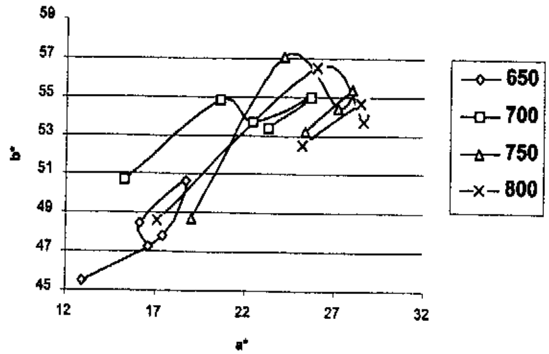

Fig. 1 Dependence $a^* - b^*$ (temp. 650 – 800 °C; 0.1 – 0.5 % chomophore)

The method of ANOVA – analysis of variance.

The analysis of variance tests the amount of selective data sets, whether it is possible to consider them as a selection from the same basic data set with particular proportions and variances. Tests are focused on research into influence of different experimental factors upon the obtained result (for instance influence of a method, an instrument, a concentration), in particular experimental diversifications — i.e. more levels of the investigated factor and the same measurement repeated several times. Divergence of measured values is caused either by accidental effects (in repeated measuring) or effects of different levels of individual factors. This method is convenient even for systems having only one measurement when the measurement is not repeated several times, indeed, the relevance of results is worse.

The base of dispersion analysis consists in decomposition of the whole dispersion of measured data into the accidental dispersion (uncontrollable effects) and the dispersion caused by individual factors or their combinations. The tested subject is then a statistical importance of ratio of both variances, i.e. whether the variance caused by accidental effects does not differ from the variance of factors significantly. Then experimental results are not influenced by these factors significantly and *vice versa*.

According to the experimental arrangement forms of the variance analysis are as follows: The easiest method is classification according to one factor (i.e. by means of the data table with columns which demonstrate different levels of the factor — for example concentration — and lines giving repetition of the same measurements). The more difficult is then double or multi-factored ANOVA with or without the repetition, with or without the interaction of factors.

Conditions of using ANOVA

The basic premise is the normality of the measured data assessment, and individual factor levels must be independent and must have the same statistical variance (homoscedasticity).

When these conditions are not fulfilled, it is possible to perform the variance analysis with help of non-parametrical tests, for instance single-factored ANOVA is replaced by Kruskal–Walis´s test, double-factored without repeating by Friedman´s test. If the data have a variable variance (heteroscedasticity), it will be necessary to use Kolmogorov–Smirnov's test or data transformation (Ref. [3]).

Experimental

The pigment system $A_{2-x}B_xO_3$, where x = 0,1; 0,2; 0,3; 0,4 and 0,5, prepared by a reaction of defined oxides being in the solid state at temperatures 650, 700, 750 and 800 °C was used. The acrylate copolymer was used as a bonding agent for the resultant pigment. Finally, the pigment was applied on a paper plate and the values of colour coordinates L^*, a^*, b^* were measured, always 10 times for each of the samples using the instrument MiniScan (HunterLab, USA). The instrument was calibrated for the white and the black standard before every measurement.

Herewith, the data matrix was obtained having 4 columns (4 temperatures) and 5×10 lines (5 different supplements of chromophores B and 10 repeated measurements of colour properties of each sample). Also the influence of the added crystallizer into the reactive mixture was tested. Five commonly used substances were chosen viz. CaF_2, MgF_2, H_3BO_3, AlF_3, KCl at three different concentrations: 1, 3 and 5 % (by wt.). Altogether three data matrixes were received (i.e. three different concentrations of the mineralizator) for three different temperatures (700, 750 and 800 °C) and five columns (i.e. five different mineralizers). Temperature 650 °C was excluded because it was not sufficient to complete reaction. Finally, the influence of individual mineralizers was tested, i.e. the data matrix for three temperatures to different mineralizer supplements.

Each of the measured values (L^*, a^*, b^*) was evaluated independently.

Results

Evaluation of the matrix was performed with help of the program EXCEL 2003 and compared with the program ADSTAT. The conclusions were the same.

Single-factored ANOVA

Available is the single-factored ANOVA with the repetition for different values of added chromophores B and one temperature — i.e. for 10-line matrix and 5 columns (supplements). Each of measured values must be evaluated independently. The conditions of the method are fulfilled. It is conclusively clear that the variances inside columns are insignifant ($F < F_{crit}$) compared with the variances between columns ($F > F_{crit}$) — i.e. the influence of concentration is significant — Table I. The research demonstrates that the reproducibilities of colour measuring are very good. Prime expectations that the anomalies in colour curves are due to incorrect measurements were not confirmed. Value b^* was tested too, but the results were the same as those of a^*, L^*).

Table I Different concentrations of chromophore B at one temperature

Parameter L^*

Anova: one factor						
Factor						
Selection	*Number*	*Total*	*Average*	*Dispersion*		
Column 1	10	652.13	65.213	0.0148		
Column 2	10	650.64	65.064	0.0102		
Column 3	10	642.46	64.246	0.0096		
Column 4	10	647.21	64.721	0.01725		
Column 5	10	587.28	58.728	0.03642		
ANOVA						
Variability source	*SS*	*Difference*	*MS*	*F*	*Value P*	F_{crit}
Between selections	301.5525	4	75.38812	4268.648	2.06e–57	2.578739
All selections	0.79474	45	0.01766			
Total	302.3472	49				

Table I – Continued

Parameter a^*

Anova: one factor						
Factor						
Selection	*Number*	*Total*	*Average*	*Dispersion*		
Column 1	10	253.26	25.326	0.0084		
Column 2	10	279.64	27.964	0.0033		
Column 3	10	271.6	27.16	0.0053		
Column 4	10	241.56	24.156	0.0186		
Column 5	10	189.66	18.966	0.01058		
ANOVA						
Variability source	*SS*	*Difference*	*MS*	*F*	*Value P*	F_{crit}
Between selections	502.7083	4	125.6771	13615.82	9.94e–69	2.578739
All selections	0.41536	45	0.0092			
Total	503.1236	49				

Double-factored ANOVA

The whole matrix was submitted to double-factored dispersion analysis with repetition — Table II. The conclusion is similar to that from single-factored testing, i.e. the influence of temperature and structure is important (all the values $F > F_{crit}$). However, it is clear that the two factors influence each other, i.e. they are in an interaction. The original question is thus solved, i.e. anomalies at curves of colour dependence are explained.

On the basis of this fact, it is necessary to modify the experiment to minimize mutual influence of factors. One of possibilities is a supplement of the mineralizer into the reaction mixture. Different mineralizers (Table III) were tested for one concentration of chromophore B (supplement 0.4).

Considering the tests mentioned above, the influence of the mineralizer decreases the factor interaction — temperature and structure of the reaction mixture. However, the addition of the mineralizer shifts individual parameters a^*, b^* and L^*, i.e. modifies colour pigment properties. The parameters do not have the same assessments, i.e. changes in composition of the reaction mixture influence parameter a^* the most and parameter b^* the least (Table III). The specified pigment must be considered seriously, i.e. which of parameters and colours are preferred.

Also tests regarding influence of quantity of the added mineralizer and the

Table II Different concentration of chromophore B vs. different temperatures

Parameter a^*

Anova: two factors with repetition (temperatures vs. composition)						
Factor	650	700	750	800	Total	
0.1 – 0.5						
Total						
Number	50	50	50	50		
Total	817.77	1072.02	1235.72	1252.07		
Average	16.3554	21.4404	24.7144	25.0414		
Variance	3.700956	12.45564	10.26783	17.95584		
ANOVA						
Variability source	*SS*	*Difference*	*MS*	*F*	*Value P*	F_{crit}
Selection	1868.33	4	467.0825	74380.14	2.00e–288	2.421843
Columns	2437.124	3	812.3746	129365.9	9.60e–300	2.654792
Interaction	305.1728	12	25.43106	4049.747	6.20e–212	1.806288
Together	1.13034	180	0.00628			
Total	4611.757	199				

Table III Addition of 3 % mineralizer at different temperatures

Parameter a^*

Anova: two factors with repetition (temperatures vs. different mineralizator)						
Factor	KCl	AlF_3	H_3BO_3	MgF_2	CaF_2	Total
700 – 750 – 800						
Total						
Number	30	30	30	30	30	
Total	790.68	463.14	550.69	200.22	677.5	
Average	26.356	15.438	18.35633	6.674	22.58333	
Variance	0.622377	0.581037	9.065031	0.665494	3.428478	
ANOVA						

Table III – Continued

Variability source	*SS*	*Difference*	*MS*	*F*	*Value P*	F_{crit}
Selection	96.51332	2	48.25666	2657.034	3.9e–109	3.063204
Columns	6771.858	4	1692.965	93215.41	3.5e–231	2.438739
Interaction	317.5449	8	39.69311	2185.521	8.5e–139	2.007635
Together	2.45185	135	0.01816			
Total	7188.368	149				

Parameter *b**

Anova: two factors with repetition
(temperatures vs. different mineralizer)

Factor	KCl	AlF_3	H_3BO_3	MgF_2	CaF_2	Total
700 – 750 – 800						
Total						
Number	30	30	30	30	30	
Total	1754.63	1708.14	1702.76	1482.19	1755.5	
Average	58.48767	56.938	56.75867	49.40633	58.51667	
Variance	0.349791	1.808568	5.206453	1.620355	1.084306	

ANOVA

Variability source	*SS*	*Difference*	*MS*	*F*	*Value P*	F_{crit}
Selection	22.97703	2	11.48852	91.86437	6.56e–26	3.063204
Columns	1723.55	4	430.8874	3445.458	8.7e–135	2.438739
Interaction	252.1547	8	31.51933	252.0346	3.20e–77	2.007635
Together	16.88304	135	0.12506			
Total	2015.564	149				

most convenient type for determined experimental system were performed.

Apart from the addition of the 3 % mineralizer mentioned above, 1% and 5% additions were studied, too. The amount of 3 % gave the best result, a smaller quantity did not indicate almost anything, higher addition did not develop any adequate improvement in the characteristics as compared with the 3 % addition of the mineralizer.

The dependences of values *a** - *b** for different concentrations of mineralizers are represented in Figs 2 – 4. Comparing the addition of 1% and 3 %, one can see that a 3 % addition of mineralizer leads to a more straight trend of the dependences mentioned.

As far as the choice of the most suitable mineralizer is concerned, boric

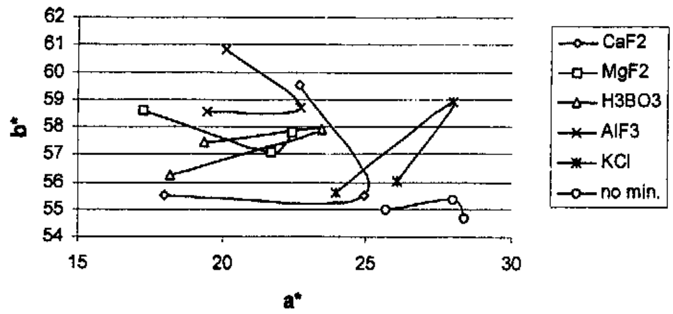

Fig. 2 Addition of 1 % mineralizer (temp. 700, 750, 800 °C, 0.4 % chromophore)

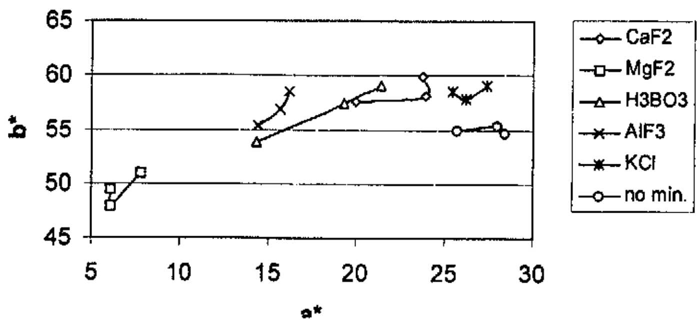

Fig.3 Addition of 3 % mineralizer (temp. 700, 750, 800 °C, 0.4 % chromophore)

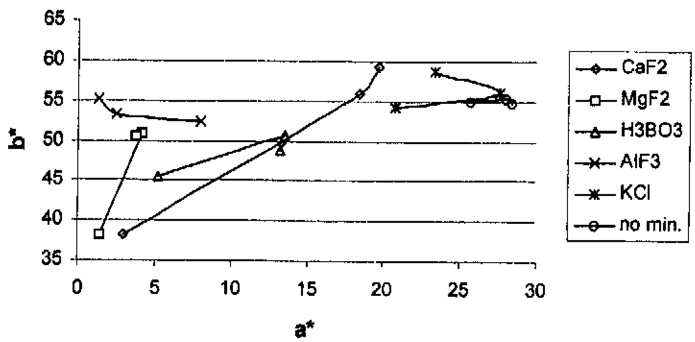

Fig.4 Addition of 5 % mineralizer (temp. 700, 750, 800 °C, 0.4 % chromophore)

acid, H_3BO_3, gave the best results: the most significant reduction in participation of the parameter interaction that influences column and line parameters. This is visible even in the graphical form – dependence a^* vs. b^* has a clear trend for boric acid.

Individual mineralizes indicate a change of the data dispersion as compared

Table IV Different concentration of mineralizer (0.01 – 0.03 – 0.05) vs. calcination temperature (700 – 750 – 800 °C) for individual mineralizers (parameter a^*)

Anova: two factors with repetition (temperatures vs. different mineralizer)				a^*	CaF_2	
Factor	0.01	0.03	0.05	Without m.		
700 – 750 – 800						
Total						
Number	30	30	30	30		
Total	655.62	677.5	411.28	820.52		
Average	21.854	22.58333	13.70933	27.35067		
Variance	8.665583	3.428478	60.05097	1.464006		
ANOVA						
Variability source	*SS*	*Difference*	*MS*	*F*	*Value P*	F_{crit}
Selection	1333.435	2	666.7177	73532.04	5.50e–170	3.080387
Columns	2884.816	3	961.6055	106055.1	3.80e–187	2.688691
Interaction	800.2472	6	133.3745	14709.83	7.80e–155	2.183657
Together	0.97924	108	0.00907			
Total	5019.478	119				

Anova: two factors with repetition (temperatures vs. different mineralizer)				a^*	MgF_2	
Factor	0.01	0.03	0.05	Without m.		
700 – 750 – 800						
Total						
Number	30	30	30	30		
Total	613.88	200.22	93.75	820.52		
Average	20.46267	6.674	3.125	27.35067		
Variance	5.34622	0.665494	1.412253	1.464006		
ANOVA						
Variability source	*SS*	*Difference*	*MS*	*F*	*Value P*	F_{crit}
Selection	108.9484	2	54.4742	4898.637	1.10e–106	3.080387
Columns	11738.77	3	3912.924	351872.8	2.80e–215	2.688691
Interaction	147.6018	6	24.60031	2212.203	1.40e–110	2.183657
Together	1.20099	108	0.01112			
Total	11996.52	119				

Table IV – Continued

Anova: two factors with repetition (temperatures vs. different mineralizer)				*a**	H_3BO_3	
Factor	0.01	0.03	0.05	Without m.		
700 – 750 – 800						
Total						
Number	30	30	30	30		
Total	610.42	550.69	319.52	820.52		
Average	20.34733	18.35633	10.65067	27.35067		
Variance	5.309875	38541	15.18883	1.464006		
ANOVA						
Variability source	*SS*	*Difference*	*MS*	*F*	*Value P*	F_{crit}
Selection	662.6921	2	331.3461	25979.06	1.30e–145	3.080387
Columns	4246.511	3	1415.504	110982	3.20e–188	2.688691
Interaction	235.7351	6	39.28918	3080.453	2.80e–118	2.183657
Together	1.37747	108	0.012754			
Total	5146.315	119				

Anova: two factors with repetition (temperatures vs. different mineralizer)				*a**	AlF_3	
Factor	0.01	0.03	0.05	Without m.		
700 – 750 – 800						
Total						
Number	30	30	30	30		
Total	623.12	463.14	119.47	820.52		
Average	20.77067	15.438	3.982333	27.35067		
Variance	2.020551	0.581037	8.749025	1.464006		
ANOVA						
Variability source	*SS*	*Difference*	*MS*	*F*	*Value P*	F_{crit}
Selection	38.6628	2	19.3314	2783.61	1.230e–93	3.080387
Columns	8796.036	3	2932.012	422192.8	1.50e–219	2.688691
Interaction	332.2112	6	55.36853	7972.749	1.70e–140	2.183657
Together	0.75003	108	0.00695			
Total	9167.66	119				

Table IV – Continued

Anova: two factors with repetition (temperatures vs. different mineralizer)				a^*	KCl	
Factor	0.01	0.03	0.05	Without m.		
700 – 750 – 800						
Total						
Number	30	30	30	30		
Total	780.03	790.68	716.91	820.52		
Average	38377	26.356	23.897	27.35067		
Variance	2.787871	0.622377	8.290367	1.464006		
ANOVA						
Variability source	*SS*	*Difference*	*MS*	*F*	*Value P*	F_{crit}
Selection	250.0794	2	125.0397	18802.44	4.70e–138	3.080387
Columns	190.0372	3	63.34574	9525.41	1.00e–130	2.688691
Interaction	130.9764	6	21.8294	3282.526	9.20e–120	2.183657
Together	0.71822	108	0.00665			
Total	571.8112	119				

with the sample without mineralizer, which is connected with thermal stability of the determined mineralizer, i.e. lower stability causes lower reproducibilities of results and therefore higher values of the dispersion. Nevertheless, the results of the dispersion analysis are not changed at all.

Conclusion

The research revealed that the final pigment colours are influenced either by firing temperature or by the quantity of the added chromophore (B). On the other hand, a problem lies in mutual interaction of both factors, which creates irregularity of the final pigment colour. This mutual action can be limited by modification of experimental conditions — for instance by addition of the mineralizer.

The 3 % addition was found as optimum. The most suitable for this particular experimental system appears to be boric acid: the mutual interaction of temperature and composition was decreased the most. Anyway, saddition of the mineralizer causes colour changes of the pigment, i.e. some of values a^* and b^* are shifted. The value a^* is affected more. It is necessary to consider the desired pigment colours, the fact, which can be predominant for a decision regarding the reaction composition and reaction conditions. By contrast, colours can be modified by this system according to needs.

The experiments are time-demanding; future research will be focused on the influence of homogenization methods of the reaction mixture, on influence of composition of the reaction raw materials. The situation is quite complicated because the experimental systems differ considerably, i.e. each of pigment types reacts differently. The same method will have to be applied also for other experimental systems, because especially this type of the mineralizer will be undoubtedly closely related with the given experimental system.

Acknowledgments

This work was supported by the Grant Agency of the Czech Republic. Pproject No. 104/05/2081.

Symbols

SS	sum of residual squares
Difference	degree of freedom
MS	SS/difference, i.e. mean of residual squares
F	actually value of Fisher–Snedecor test
F_{crit}	critical value of Fisher–Snedecor test (tabelled)
P	probability of rejection of zero hypothesis (selections are from the same data)

References

[1] Žára J., Beneš B., Sochor J., Felkel P.: *Modern Computer Graphic* (in Czech), Computer Press, Brno, 2004.
[2] Meloun M., Javůrek M.: *Chemometrics I* (in Czech), VŠCHT Pardubice, 1986
[3] Kubanová J.: *Statistical Methods for Economical and Technical Practice* (in Czech), Statis, Bratislava, 2003.