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The effect of the cation composition on the synthesis and properties of ultramarine blue

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Abstract

The effect of potassium cations on the shade of the ultramarine blue pigment system has been investigated through analysis of commercial materials, ion exchange reactions of sodium-form ultramarine blue and a detailed study of the effect of adding potassium sources to ultramarine precursor mixtures. Incorporation of potassium cations has the result of producing redder shade material and the replacement of around 20% of the sodium in the standard reaction mixture produces the optimised red-shade pigment. The origin of this hue control may be a direct effect, involving interaction of potassium ions with the ultramarine blue structure and the S_3^- chromophore or, more likely, potassium ions aids the stabilisation of S_3^- within the sodalite framework during the ultramarine blue formation process. In the commercial process, the role of the potassium source in red shade formation may be performed by the incorporation of potassium-rich feldspar additives.

Keywords: Ultramarine; Potassium; Shade control; Ion exchange

1. Introduction

Since its original manufacture in the 1830s, ultramarine blue has remained an important commercial inorganic pigment [1]. The structure of ultramarine blue, general formula $Na_{8-x}[SiAlO_4]_6.[S_2,S_3,SO_4,Cl]_{2-x}$, consists of an aluminosilicate framework, constructed from β-type (or sodalite) cages, containing sodium cations and anionic, mainly sulphur based, groups, (Fig. 1) [2,3]. Current opinion is that the two dominant sulphur species in ultramarine blue are S_3^- and, to a lesser degree, S_2^-. The S_3^- polyanion radical is responsible for the strong absorptions in the visible region, thus producing the intense blue colour [4,5]. The aluminosilicate framework imparts high chemical stability and thermal stability to the pigment and to the otherwise reactive sulphur species. Previous work on the synthesis and on the structure of ultramarine blue includes that of Tarling and Barnes, who investigated the structure and formation of ultramarine blue using X-ray diffraction and solid state NMR methods [3,6,7], Clarke who used Raman spectroscopy to probe the nature of the chromophore in various ultramarines [5] and, more recently, Demortier et al. who used ESR methods to quantify the level of S_3^- in ultramarines synthesised under various conditions [8].

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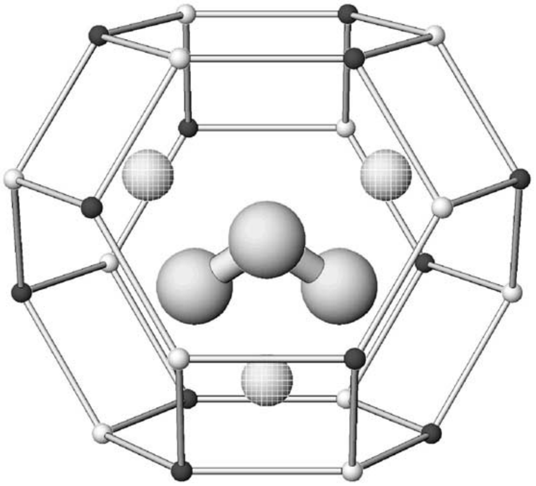

Fig. 1. The ultramarine blue structure showing a single sodalite cage containing an S_3^- unit. Na ions are shown as hatched grey spheres and for the framework only the tetrahedral atoms are shown with alternating Si (dark grey) and Al (pale grey).

The raw materials used in ultramarine blue manufacture are china clay (mainly kaolin, $Al_2Si_2O_5(OH)_4$, but also containing significant levels of quartz, feldspars and micas), feldspar additives, typically $MAlSi_3O_8$ (M = Na, K), sulphur and a reductant, such as pitch. The kaolin or china clay is dehydrated prior to use. The reactants are mixed and then formed into pellets or bricks under pressure. In a typical reaction, the bricks are heated initially to approximately 800 °C for a period of 4–5 days and then allowed to cool, except during an intermediate oxidation stage, over a period of 3 weeks. The chemical reactions are complex and generally take place in three distinct stages. The first occurs under reducing conditions where sodium sulphide is formed by the reaction of the reductant, sodium carbonate and sulphur components. The second is the formation, at high temperatures, of primary ultramarine with construction of the sodalite cage. During the final cooling stage, an oxidising gas, air or sulphur dioxide, is admitted to the reaction chamber and primary "green" ultramarine is converted through an oxidation process to the blue pigment, ultramarine. The main product after furnacing is brilliant blue but contains around 20% of sodium sulphate, feldspars, quartz and iron sulphide, particularly on the outsides of the bricks. The soluble salts are removed by washing with sodium hydroxide. The ultramarine blue is then wet ground, cleaned through floatation methods and then settled in tanks to produce various grades of ultramarine blue.

The exact shade of the ultramarine blue synthesised is of importance in determining the quality of the product and, hence, its applications. Conventionally extremes of "blue" may be obtained from "green" shade material to "red" shade material and considerable effort has been applied to controlling this ultramarine shade formation and synthesis of the preferred red shade. The manipulation of the Si:Al ratio as a method of achieving shade control has been discussed [7]. The commercial formulations of green and red shade materials differ mainly in that red shade formulations contain silicon rich additives, such as orthoclase feldspar $KAlSi_3O_8$, which are believed to produce a silicon rich framework in the ultramarine blue product i.e. $Na_{8-y}[Al_{1-x}Si_{1+x}O_4]_6.[S_3^-,S_2^-]$. Shade control using this type of compositional adjustment has met with some success and typical factory formulations which generate red and green shades are given in Table 1, demonstrating the efficacy of this methodology. However, naturally occurring ultramarine (Lapis Lazuli), with a good red shade, has a silicon: aluminium ratio of 1:1 with an ordered framework of alternating silicon and aluminium, i.e. no excess silicon [7].

Other compositional features of the product that could also control the shade include the S_3^-/S_2^- ratio and the cation content. While S_3^- is the key chromophore within the ultramarine blue system S_2^- is usually present and its UV/VIS spectrum indicates that this species imparts a yellow colour to ultramarine, though the absorption coefficient

Table 1
Typical commercial red and green shade formulations

'Green' shade	Mass%	'Red' shade	Mass%
Meta-kaolin	32.0	*Meta*-kaolin	30.0
Feldspar	0.0	Feldspar	7.0
Sodium carbonate	29.0	Sodium carbonate	27.0
Sulphur	34.5	Sulphur	33.0
Reducing agent	4.5	Reducing agent	3.0

of this species is much weaker than S_3^- [4,5]. Hence the ratio of S_3^- /S_2^- would be expected to control ultramarine blue pigment shade with high levels of S_2^- imparting a green shade, though it is unclear why addition of feldspars to the reaction mixture would necessarily influence the ratio of the two polysulphide species. While ultramarine blue is normally represented by the formula $Na_{8-x}[AlSiO_4]_6[S_3,S_2]_{2-x}$, that is a pure sodium form, it is clear that the cation content of sodalite materials can vary considerably and be modified through ion exchange, either in solution or in melts [9]. The cation composition can also have a marked effect on the pigment colour; for example exchanging the sodium ions of ultramarine blue with silver leads to a green product. Clearly the cations contained within the sodalite cages can have a major effect on ultramarine blue shade, either directly in terms of the ultramarine composition and their interaction with the chromophores or, perhaps, indirectly through modifying during the ultramarine blue synthesis the framework composition or the S_3^- /S_2^- ratio. In this paper we describe studies of the effect of potassium ions in the synthesis of ultramarine blue, from kaolin, on the product's blue shade.

2. Experimental

2.1. Cation analysis of commercial pigments

Scanning electron microscopy (SEM) was performed using a Jeol JSM-6400 in conjunction with a TRACOR Series II energy dispersive X-ray analysis (EDAX) system. Samples of commercial raw ultramarine products, green and red shades, from the Holliday Pigments, Morley Street, Hull site were subjected to EDAX analysis. For each shade several different samples were analysed using various spot/area sizes and the results averaged to give the cation and sulphur contents.

2.2. Laboratory synthesis of ultramarines. Effect of sodium content

Meta-kaolin (30 g), sulphur (33 g) and high melting point oil (3 g) were combined with various quantities of sodium carbonate to the compositions summarised in Table 2. The kaolin used throughout this work was a high purity material (>99%). These were dry ground for 15 min using a motorised pestle and mortar then transferred to a Z-blade mixer with steam jacket attachment for 1 h at 120 °C. The materials were then quickly pressed into 20.0 g pellets using a 30 mm SPECAC die (10 tonnes, 1 min) and marked for identification. The reactant pellets were housed in a 250 ml clay crucible with the lid sealed by furnace cement. This was then placed in a large silicon carbide crucible and the cavity between the two was filled with 200 g of powdered raw ultramarine mix (factory red shade); the function of this excess material is to model the conditions at the centre of the large ultramarine bricks used in the commercial process while allowing clean access to the materials of interest for gas treatments and product separation. The lid of the silicon carbide crucible was sealed with furnace cement and the mullite or clay gas inlet tube fitted directly through both lids and the crucible was left to dry for 24 h. The crucible was heated to 750 °C at 5 °C min^{-1} and held at this temperature for 960 min before cooling at 5 °C min^{-1} to 450 °C. SO_2 gas was admitted at this point through the mullite inlet tube at a rate of (0.1 l min^{-1}, 1440 min). The system was then allowed to cool to room temperature.

The product pellets were extracted from the surrounding mix and then broken up using a mechanical pestle and mortar for 1 min. The powder was then boiled in a 10% NaOH solution for 30 min to remove excess sulphur and sulphides. The raw pigment was washed with distilled water (200 cm^3 ×4) and portions retained for powder X-ray diffraction (PXD) and colour testing.

Table 2
The effect of sodium variation in raw materials upon the hue of products; the composition of the remainder of the reaction mixture is given in the main text

Na_2CO_3 /g	$L\pm0.5$	$C\pm0.5$	$h^*\pm0.5$
29	72.9	24.2	265.3
28	71.7	27.3	265.6
27	71.6	25.9	266.2
26	70.0	29.2	266.7
25	70.7	29.2	266.8

The diffraction data were collected on a Siemens D5000 Diffractometer, employing monochromated Cu-$K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å). Colour measurements were performed at Holliday Pigments Ltd. in Hull using a Macbeth Colour Eye 7000 colorimeter employing the CIELAB/LCH colour spaces.

2.3. Laboratory synthesis of ultramarines. Effect of potassium cations

Meta-kaolin (30 g), sulphur (33 g), high melting point oil (3 g) and sodium carbonate (25 g) were combined with small quantities of potassium carbonate as summarised in Table 3. Materials were processed using the laboratory scale method describes above and products characterised as before by PXD and colour measurements. Attempts to increase the potassium content to very high values, 10–20 g of potassium carbonate, led to significant levels of impurities in the products and poor quality pigment material.

Table 3
The derived colour parameters for an isolated potassium doping experiment using the same fixed formulation parameters; the composition of the remainder of the reaction mixture is given in the main text

K_2CO_3 /g	$L\pm0.5$	$C\pm0.5$	$h^*\pm0.5$
0	72.2	25.7	265.9
1	70.2	29.2	266.7
2	69.1	30.9	266.5
3	68.8	31.8	268.4
4	68.0	32.7	267.7
5	67.5	33.3	269.2

2.4. Laboratory synthesis of ultramarines. Control of sodium and potassium ion content

A matrix of ultramarine furnacings was carried out with the standard laboratory technique to investigate the effect of simultaneously changing the sodium and potassium levels on the shade of finished ultramarine blue products. The formulations used were similar to those listed previously; the experiment was not designed to probe any particular optimum formulation or to maintain a specific stoichiometry of one reactant but to cover a wide area of composition space in terms of Na^+ and K^+ levels. The formulation consisted of *meta*-kaolin (30 g), sulphur (33 g) and high melting point oil (3 g) combined with differing amounts of sodium and potassium carbonate as summarised in Table 4. Note that this series of experiments was run separately from the single sodium and potassium studies. Some differences in product properties for similar composition were apparent between experiments which may be associated with uncontrollable variables within reaction chemistry, such as the level of sulphur loss; trends within the individual runs were, however, fully consistent.

2.5. Solution ion exchange

Samples of ion exchange ultramarine blue were prepared from a commercial green shade ultramarine. Ion exchange was achieved by stirring the parent materials in solutions of KNO_3 (60 °C, 24 h) at various concentrations between 10^{-3} and 1 M; for higher exchange levels the reaction was repeated several times with 1 M KNO_3. The modified materials were then filtered by suction through a sintered glass filter (grade 3) and washed with distilled water (4×20 cm^3). The degree of ion exchange was determined, following dissolution of the product in bromine, by flame photometry with the potassium contents determined. Infra-red data were collected for each sample from Nujol mulls (CsI) on a Perkin Elmer 983G Infrared Spectrometer. Powder X-ray diffraction data were collected to determined changes in the lattice parameter following ion exchange.

3. Results

3.1. Cation analysis of commercial pigments

EDAX analysis of raw ultramarine blue products from the Morley Street site gave the following cation and sulphur stoichiometries: red shade $Na_{6.2}K_{0.5}[AlSiO_4]_6(S_3^-)_{0.7}$, green shade $Na_{6.5}K_{0.2}[AlSiO_4]_6(S_3^-)_{0.65}$; values obtained for aluminium, silicon and oxygen were close to nominal and no difference, within experimental error, was found in the silicon and aluminium contents for the red and green shades. A typical percentage error on the potassium, sodium and sulphur contents from this technique without calibration is ±5% and variation in measurements for different samples and areas of samples was ±3%. From the Na:K ratio, it is clear that red shade samples have significantly higher potassium cation content than green shade, slightly less sulphur was found in green shade material which could be consistent with a higher level of S_2^- over S_3^-[5].

Table 4
Colour values derived from the matrix of Na_2CO_3 and K_2CO_3 formulations. Weights are given in 100 g of reaction mixture; the composition of the remainder of the reaction mixture is given in the main text

K_2CO_3 /g	Na_2CO_3 /g	$L \pm 0.5$	$C \pm 0.5$	$h^* \pm 0.5$
0.00	29.00	71.8	20.4	258.9
0.00	28.00	70.4	22.6	259.5
0.00	27.00	71.2	22.0	259.7
0.00	26.00	74.0	23.4	259.8
0.00	25.00	70.9	21.2	259.9
0.00	24.00	73.4	20.9	260.3
0.00	23.00	71.6	22.8	260.9
1.00	29.00	72.5	21.3	261.2
1.00	28.00	74.3	20.6	261.3
1.00	27.00	72.7	21.8	261.4
1.00	26.00	73.4	21.7	261.8
1.00	25.00	73.6	22.0	261.9
1.00	24.00	72.5	23.1	262.0
1.00	23.00	75.0	19.5	262.2
2.00	29.00	73.5	21.8	262.4
2.00	28.00	73.5	20.2	262.4
2.00	27.00	69.4	27.8	262.4
2.00	26.00	70.7	25.7	262.4
2.00	25.00	72.6	21.8	262.5
2.00	24.00	70.4	27.2	262.5
2.00	23.00	70.2	22.5	262.5
3.00	29.00	72.6	22.6	262.5
3.00	28.00	73.0	23.1	262.6
3.00	27.00	73.2	23.3	262.6
3.00	26.00	71.5	23.5	262.6
3.00	25.00	74.2	20.5	262.8
3.00	24.00	72.6	23.6	262.9
3.00	23.00	72.0	20.7	262.9
4.00	29.00	72.1	23.7	262.9
4.00	28.00	71.0	23.5	263.0
4.00	27.00	73.5	20.2	263.0
4.00	26.00	75.4	20.7	263.5
4.00	25.00	72.5	24.6	263.6
4.00	24.00	75.8	19.8	263.6
4.00	23.00	73.1	22.7	263.7
5.00	29.00	74.0	21.2	264.1
5.00	28.00	72.1	23.4	264.1
5.00	27.00	72.6	24.8	264.1
5.00	26.00	70.3	27.3	264.1
5.00	25.00	71.8	24.7	264.2
5.00	24.00	73.0	22.4	264.2
5.00	23.00	73.0	21.3	264.3
6.00	29.00	70.8	26.9	264.4
6.00	28.00	73.3	24.5	265.2
6.00	27.00	73.2	25.4	265.9
6.00	26.00	73.4	24.3	266.0
6.00	25.00	73.7	23.9	266.6
6.00	24.00	73.9	18.9	267.1
6.00	23.00	72.1	25.9	267.3

3.2. *Effect of sodium content. Synthesis of sodium ultramarines*

Ultramarine products were confirmed to be phase pure by PXD traces showing the presence of a single cubic phase $a = 9.10$ Å, no additional reflection was observed indicating levels of impurities, such as nepheline $NaAlSiO_4$, were below 5%. The precise colourimetric parameters of each material were then measured and are summarised against the original formulation for each sample in Table 2; data are plotted in Fig. 2. The reddest shades, i.e. those with the highest hue (h^*) values, were prepared from formulations which had low sodium contents, though the products were similar across the compositional range with a small range of h^* values, Δh^*, of 1.53. This value is outside experimental errors but not that significant with respect to variations in commercial pigments; for example the difference in h^* values between commercial red and green shades is approximately 5–10 units. The materials became weaker pigments as the hue decreased (low chromacity and high luminescence) probably reflecting a reduction in the overall level of S_3^- anions in such materials.

3.3. *Effect of potassium ions. Synthesis of potassium containing ultramarines*

Colourimetric parameters for this experiment were measured and plotted against the original formulation for each sample as listed in Table 2, and plotted in Fig. 3. The range of hue values across all formulations was reasonably large

($\Delta h^* = 3.33$). The same type of trends in h^* were apparent from potassium variation as were the case for sodium variation with higher cation contents producing redder shades. Pigment strengths were enhanced by the presence of the potassium containing additives, small quantities of potassium (1% K_2CO_3) resulting in large positive chromacity changes $\Delta C = +3.5$ compared to the potassium free material. Δh^* across all compositions still only spans a narrow range compared to normal

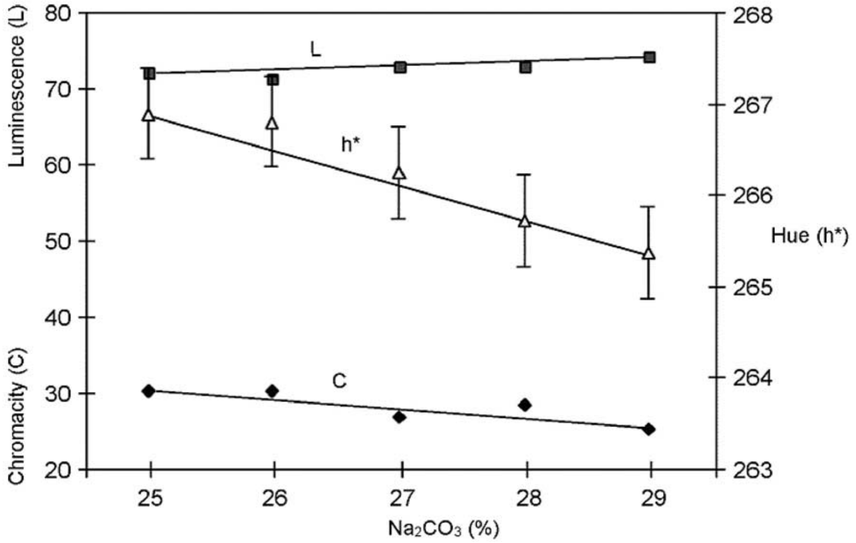

Fig. 2. The effect of sodium content in the reaction mixture on the derived colour parameters of the ultramarine blue product.

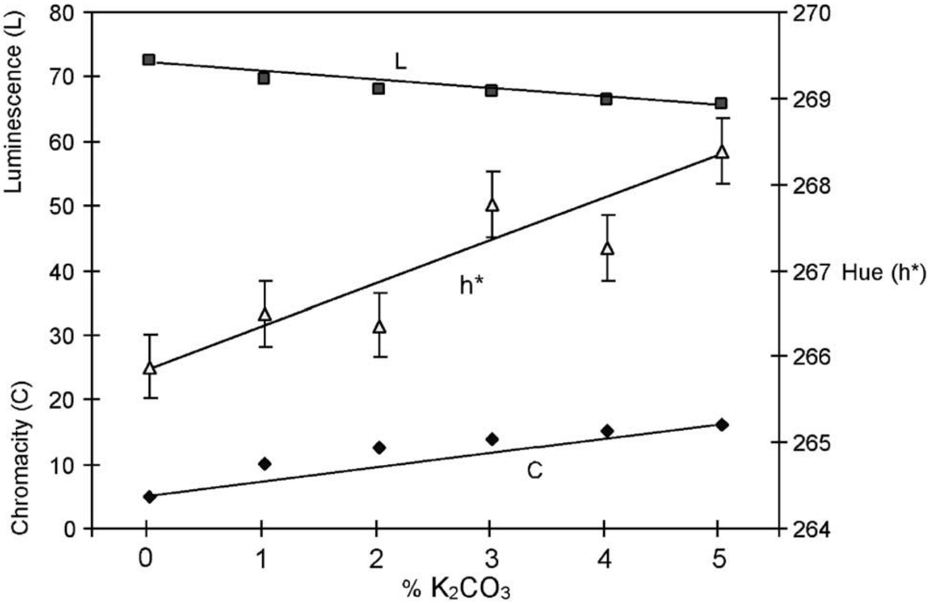

Fig. 3. The effect of potassium content in the reaction mixture on the derived colour parameters of the ultramarine blue product.

industrial preparations but the values are at the upper end of the commercial pigment range and higher than the pure sodium forms. It was noteworthy that material synthesised with the higher potassium levels still produced ultramarines that were identical in terms of phase purity, from powder X-ray diffraction analysis ($a \sim 9.12$Å), to the control, purely sodium based material; only at very high levels of potassium, over 8 g, did significant levels of impurities arise.

3.4. Effect of sodium and potassium cations. Synthesis of mixed sodium and potassium containing ultramarines

The key parameter for these materials was the hue (h^*) the results for which are given below in Table 5 and Fig. 4. No significant trends in luminescence or chromacity were apparent. Materials prepared from mixtures rich in potassium and lower in sodium gave significantly higher hue values with a large resultant range of h^* values ($\Delta h^* = 8.42$). These results are discussed in detail below.

3.5. Solution ion exchange

Analysis of the products showed that up to half the sodium ions in ultramarine blue may be exchanged with potassium yielding products of the compositions $Na_{8-x}K_x[AlSiO_4]_6(S_3^-)_{0.7}$, $0 < x < 4$. Higher potassium ion contents lead to monotonically increasing lattice parameters reaching 9.23Å for the greatest levels of exchange. The series of samples produced showed a gradual increase in h^* with increasing potassium ion-exchange into the ultramarine structure, Fig. 5. The small changes, $\Delta h^* = 1.52$, are consistent with a transformation of the parent material into a redder material. The magnitude of the overall change remains outside of experimental errors and is significant with respect to product specifications though lower than the variations seen when potassium is involved directly in the ultramarine synthesis.

Infra-red spectra collected from the ion exchanged materials were consistent with those reported previously for ultramarine blues with three absorptions between 200 and 600 cm^{-1} that can be associated with the S_3^- units. These data are summarised in Table 5. As the potassium content increases towards the maximum obtainable, through ion exchange at $Na_4K_4[AlSiO_4]_6.[S_2^-,S_3^-]$, all the vibrational frequencies decrease monotonically indicating some interaction between the cation and the sulphur groups. This may be a result of changes in the S…M interactions due to different bond lengths and electron distributions or may be directly associated with changes in the S_3 unit geometry. For a bent triatomic the bond angle may be calculated from the vibrational frequencies using the method of Herzberg [10] and the results of such calculations are summarised in Table 5. While the errors on such calculations are probably significant there is an indication that the S–S–S bond angle is decreasing as the potassium level rises.

Table 5
Potassium contents, colour properties and vibrational frequencies and for ion exchanged materials

K^+	$L \pm 0.5$	$C \pm 0.5$	$h^* \pm 0.5$	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})	Calculated angle[ab]
0.19	71.4	30.5	260.6	549.1	259.7	600.3	106
0.39	71.3	30.4	260.8	548.8	259.6	599.3	106
1.10	71.2	30.8	261.1	548.1	259.8	597.4	106
2.26	71.4	30.6	261.5	546.8	259.3	593.6	106
2.51	71.2	30.2	261.6	546.4	259.2	592.6	106
4.02	71.3	30.6	262.2	545.1	258.3	588.7	105

S–S–S bond angles were calculated from the ν_1 (symmetric stretch), ν_2 (bending) and ν_3 (asymmetric stretch) vibrational frequencies (± 0.5) using the method of Herzberg [10].

[a] $\omega^3 - \left(1 + \frac{2m_y}{m_x}\right)\frac{\left(\nu_1^2+\nu_2^2+\nu_3^2\right)}{\nu_1^2\nu_2^2}\omega + 2\left(1 + \frac{m_y}{m_x}\right)\left(1 + \frac{2m_y}{m_x}\right)\frac{\nu_3^4}{\nu_1^2\nu_2^2} = 0.$

[b] $\varpi = 1 + \left(\frac{2m_y}{m_x}\right)\sin^2\alpha.$

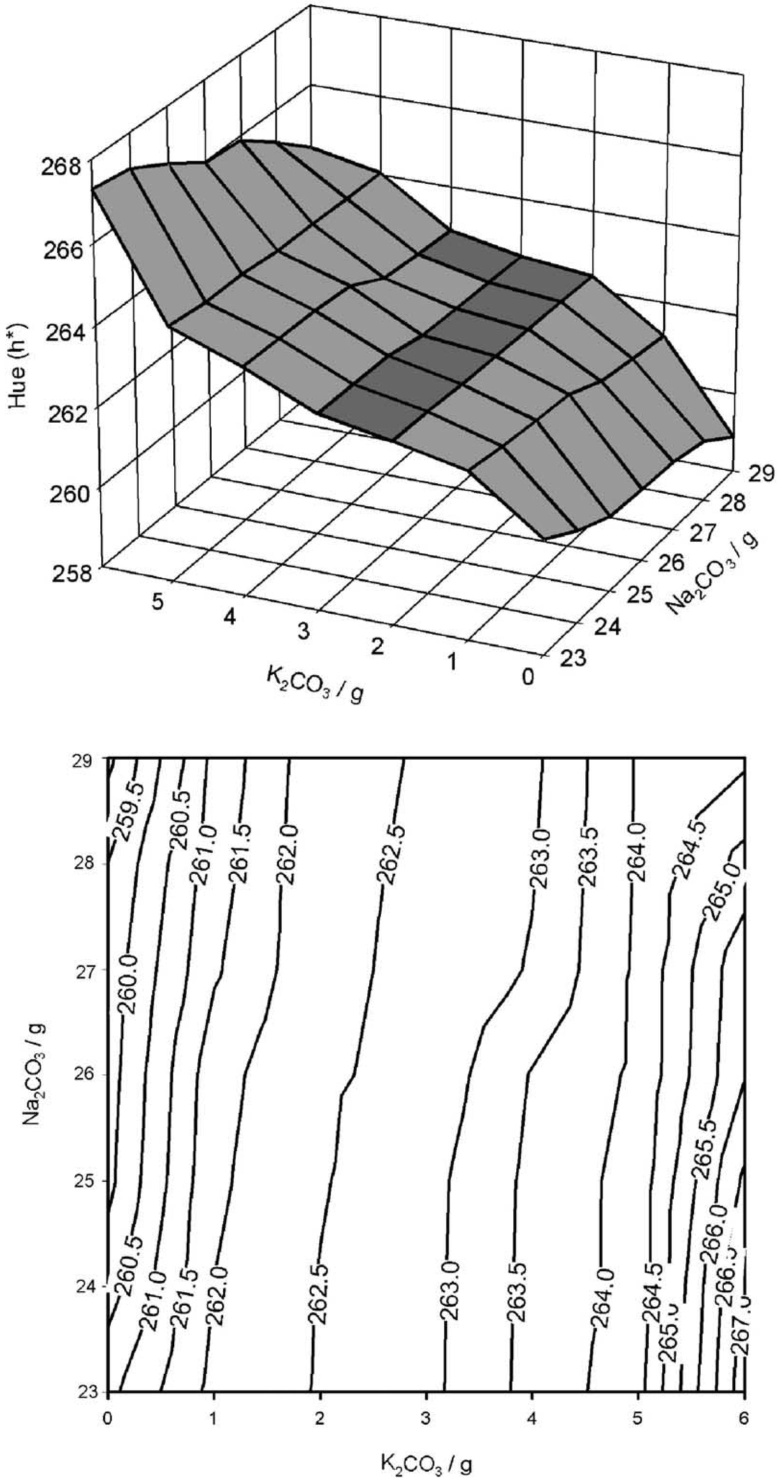

Fig. 4. A surface plot and contour plot of the derived hue values from the Na_2CO_3/K_2CO_3 doping experiments.

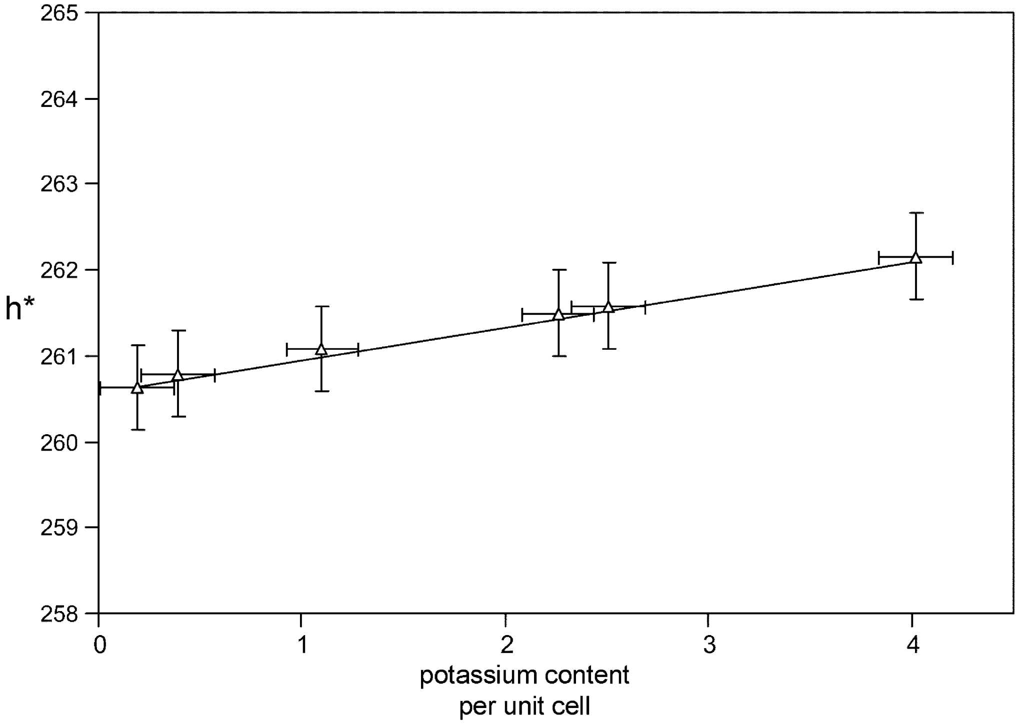

Fig. 5. Pigment hue (*h**) plotted against potassium content for materials modified by solution ion exchange.

4. Discussion

Potassium has never previously been considered to be amongst the important constituents in ultramarine blue formulations. In the industrial process potassium can be derived from the aforementioned feldspar ($KAlSi_3O_8$) either as an additive or present in commercial clays and any mica impurities which are present in a clay. Analysis of typical clay samples used in ultramarine blue manufacture show an overall, average potassium ion content of 3–4%, derived from the non-kaolin sources. In these experiments the potassium was added in a controlled manner as K_2CO_3 either replacing or adding to the sodium carbonate normally present in the reaction mixture.

The results show that addition of potassium sources to the ultramarine reaction mixtures has a significant and reproducible effect on the ultramarine product shade in that red shades are produced. Generally higher levels produce redder shades especially when the potassium replaces sodium in the reaction mixture. Hence the reddest shades obtained were for formulations consisting of ~23 g of sodium carbonate and ~6 g of potassium carbonate. Larger levels of potassium, at around 10–15 g K_2CO_3 and 10–15 g Na_2CO_3, lead to increased levels of impurities in the ultramarine products.

A similar, but less marked, control of pigment shade may be obtained through ion exchange reactions where potassium directly replaces the sodium in the sodalite cavities. This work indicates that while the interaction of the potassium ions with the polysulphide anions can modify the absorption spectrum of this species this mechanism is unlikely to be the origin of the larger changes in hue values obtained by adding potassium into the ultramarine reaction mixture. That is the hue change obtained on ion exchange was much smaller, even for 50% replacement of sodium by potassium, than obtained in the direct synthesis procedure. Analysis of the potassium contents (using EDAX) of some of the ultramarines produced with potassium added to the reaction mixture would support this assertion, in that potassium levels remain in the range $Na_{8-x}K_x[AlSiO_4]_6(S_3^-)$, $0 < x < 1$, far less than that required for the (small) hue changes observed in the exchange process.

It is more likely that the presence of potassium ions in the reaction process modifies the nature of the S_3^- group formation. Possibilities may include a stabilisation of S_3^- over S_2^- units in the presence of potassium or for example the formation of larger sodalite cavities with the larger potassium ion and thus more ready incorporation of the larger triatomic species.

5. Conclusions

The presence of potassium in the ultramarine systems seems to have a major role in controlling the shade of the blue pigment facilitating the formation of the red shade. This may be a result of modifications to the reaction chemistry during the manufacturing process, or the incorporation of potassium into the sodalite cage modifying the S_3^- absorption spectrum or most likely both.

It is likely that the addition of feldspars to the ultramarine blue reaction mixture in the commercial process which consists mainly of potassium based materials such, as orthoclase/sanidine $KAlSi_3O_8$, performs the role of potassium addition rather than the originally perceived role of adding silicon. The commercial reaction product still contains feldspar, and at appreciable levels - up to 15%, but in sodium form, $NaAlSi_3O_8$, the potassium becoming incorporated into the ultramarine blue product. It seems that a far better way of obtaining red shade ultramarine blue commercially would be through the use of a clean potassium source such as potassium carbonate.

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