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Effect of Temperature on Chromaticity Coordinates Over a 700° Range: A Study of Alkali Metal Uranates

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ABSTRACT

The diffuse reflectance spectra of the thermochromic alkali metal (Li, Na, K) mono- and diuranates have been recorded from room temperature down to nearly −200°C, and additionally for the potassium uranates up to 500°C. The colours, ranging from yellow to red, were characterised using the CIELAB and CIELUV systems. An essentially linear relationship was found between chromaticity co-ordinates and temperature, provided no physical or chemical reaction occurred. Thermochromaticity has previously only been examined between ambient and 130°C, but it is here established that the colours of thermochromic materials can be predicted outside the experimentally measured range. The solid state reaction $xM_2UO_4 + (x-1)H_2O \Longleftrightarrow M_2O(UO_3)x + (2x-2)MOH$, *where* $x > 1$ *and* $M \neq Li$, *was also followed by recording their diffuse reflectance spectra, at controlled humidity levels at room temperature. The reaction proceeds more readily as the radius of M increases, and the β form of* Na_2UO_4 *was found to be more hygroscopic than the α form. © 1998 Elsevier Science Ltd. All rights reserved*

Keywords: alkali metal uranates, diffuse reflectance spectra, visible spectra, chromaticity co-ordinates, thermochromism, hydrolysis.

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INTRODUCTION

The preparation and properties of the alkali metal mono- and diuranates, including their thermochromism, (yellow to red), were first reported towards the end of the last century. However, since that time, for over one hundred years, their chromatism has not been investigated. This study seeks to repair that omission, extend the common temperature range for diffuse reflectance measurements from around 100 to 700° and follow the effect of temperature upon chromaticity co-ordinates. In addition, since some monouranates are slowly hydrolysed in moist air to polyuranates, their colour and chemical change are also monitored and analysed using diffuse reflectance spectroscopy. Uranates are insoluble in water and most other solvents, and chemically resemble the chromates widely used as pigments. Indeed, sodium diuranate has been used in the past as a pigment ('uranium yellow'), in glazes used in the first half of the century for porcelain decoration. A range of colours was obtained by varying the chemical composition of the glazes, to give green, yellow, ivory, orange, red and vermilion colours [1–3]. The diuranate content of the initial mixture was 1 to 8% but could reach up to 20%.

Zimmermann first reported the thermochromism of sodium and potassium diuranates in 1881, noting a reversible change on heating from orange-yellow to deep red for the sodium compound and deep blood-red for potassium diuranate [4, 5]. However, the first report of a uranate and its colour was by Berzelius [6] in 1824. In the last century and the early years of this, the uranates prepared may not have been fully identified with regard to the various mono-, di- and triuranates now known, and this is one possible reason for the disparity in the colours claimed. Table 1 shows the colours reported, their (claimed) formulae and the year of publication.

This variation in reported colour is nowadays eliminated by first preparing the various uranates in the pure form (using reliable methods more recently established), analysing them (for necessary confirmation), and then characterising them using a uniform system for colour description.

Many other properties of uranates have been well studied during the second half of this century but some data in the literature are still not consistent, for example, the hydrolysis of uranates. Cordfunke and Loopstra [19] have reported that sodium monouranate is 'more or less hygroscopic' while Hoekstra [30] has stated that it was 'extremely hygroscopic'. Monouranates may react with moisture to form diuranates or similar compounds [31, 32] according to eqn (1)

$$2M_2UO_4 + H_2O \Longleftrightarrow M_2U_2O_7 + 2MOH \qquad (1)$$

TABLE 1
Reported Colours of Alkali Metal Uranates M_2UO_4 and $M_2U_2O_7$ (M = Li, Na, K)

Compound	*Colour*	*First author, year and reference no.*
Li_2UO_4	yellow-orange	Toussaint (1974) [7]
	orange-yellow	Guiter (1939) [8]; Efremova (1961) [9]; Spitsyn (1961) [10]; Prigent (1965) [11]
$Li_2U_2O_7$	yellow	Toussaint (1974) [7]
Na_2UO_4	yellow	Drenckmann (1861) [12]; Lange (1967) [13]
	golden yellow	Ditte (1882) [14]; Ditte (1884) [15]
	reddish yellow	Michel (1890) [16]
	greenish yellow	Ditte (1882) [14]; Ditte (1884) [15]
	green-yellow	Lide (1992) [17]
	orange-yellow	Spitsyn (1961) [10]; Prigent (1965) [11]; Viltange (1960) [18]
	orange	Cordfunke (1971) [19]
	red	Lide (1992) [17]
$Na_2U_2O_7$	yellow	Patera (1849, 1853, 1854, 1856) [20]; Frondel (1956) [21]
	orange-yellow	Zimmermann (1881) [4]; Zimmermann (1882) [5]; Cordfunke (1971) [19]; Fujino (1983) [22]
	orange	Gasperin (1986) [23]
	light brown	Toussaint (1974) [7]
K_2UO_4	greenish yellow	Ditte (1882) [14]; Ditte (1884) [15]
	orange-yellow	Montignee (1947) [24]; Martin (1951) [25]; Efremova (1961) [26]; Spitsyn (1961) [10]; Prigent (1965) [11]; Lange (1967) [13]; Keller (1972) [27]; Lide (1992) [17]
$K_2U_2O_7$	orange-yellow	Zimmermann (1881) [4]; Zimmermann (1882) [5]
	orange	Alpress (1968) [28]; Jove (1988) [29]
	brick red	Berzelius (1824) [6]

In eqn (1) M is limited to lithium and sodium; rubidium and cesium uranates react to form polyuranates with compositions between tri- and tetrauranates [32]. However no information on the hydrolysis reaction of potassium monouranate has been reported, and hence it is of interest to establish if it forms exclusively the diuranate, or if higher uranates are (additionally) formed.

Because mono- and diuranates have different colours, this hydrolysis reaction can readily be studied by diffuse reflectance spectroscopy. Unfortunately, no diffuse reflectance or absorption spectra of alkali metal uranates have been previously reported; only Krol [33] has analysed the excitation spectra of Li_2UO_4, and so such spectra are reported for the first time in this paper, together with the effect of temperature upon the chromaticity coordinates of the uranates unaffected by moisture.

EXPERIMENTAL

Synthesis of the uranates

Lithium, sodium and potassium mono- and diuranates, M_2UO_4 and $M_2U_2O_7$, M = Li, Na or K, were prepared using standard procedures, which involved heating stoichiometric mixtures of U_3O_8 with the corresponding alkali metal carbonate in air [19, 22, 30, 34]. A mixture of uranium oxide and the alkali carbonate was thoroughly ground, slowly heated in an alumina crucible to 800°C for 7 h, slowly cooled and the solid reground. The mixture was then heated again and the cycle repeated four times, after this the reaction was complete and a single phase was obtained. X-ray powder diffraction measurements (Philips PW1710) and IR spectroscopy (KBr) (Perkin–Elmer 457 spectrophotometer) were used to characterise the uranates.

The $\alpha \rightarrow \beta$ phase transformation of sodium monouranate is reported to occur at around 900–920°C [19, 34] and consequently we anticipated that the synthetic procedure and temperature used would yield pure α-Na_2UO_4. X-ray diffraction and IR analysis, however, showed that, although the product was predominantly α-Na_2UO_4, it contained noticeable amounts of the β-form. When the synthesis procedure was repeated, but keeping the temperature at 700°C, X-ray powder diffraction and IR spectra confirmed the product as pure α-Na_2UO_4.

Diffuse reflectance spectra

Diffuse reflectance spectra were measured using a computer controlled fibre optic spectrophotometer [Guided Wave Analyser (GWA), Model 200]. Light was conveyed to and from the sample using the 6:1 reflectance probe in which the single central sending fibre is surrounded by six returning fibres. Lithium fluoride (BDH, extra pure) was chosen as reference since it has been reported that LiF reflects between 10 and 20% more of the incident light than the generally used magnesium oxide [35]. The absence of any possible differences between absorption spectra measured in solution and those obtained from powdered solid samples was established using the chemically similar alkali metal mono- and dichromates; no differences in their profiles were detected.

Diffuse reflectance spectra at different temperatures

Figure 1(A) and (B) shows a schematic drawing of the apparatus used for recording spectra below and above room temperature. The sample temperature was constantly recorded, using a thermocouple positioned close to the

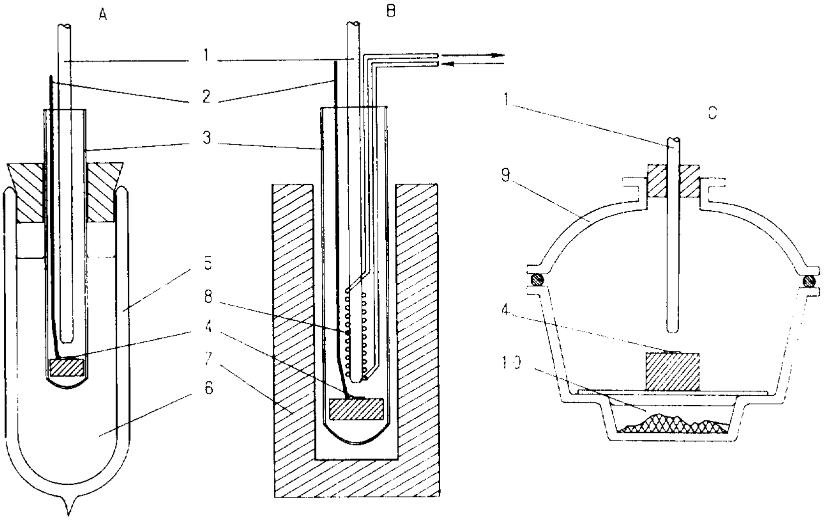

Fig. 1. Schematic diagram of the apparatus assembly used for measuring diffuse reflectance spectra at temperatures (A) below or (B) above ambient, and (C) at controlled humidity. 1, optical probe; 2, thermocouple; 3, Pyrex glass tube; 4, sample; 5, Dewar flask; 6, coolant (liquid N_2, or solid CO_2 in iso-propanol); 7, furnace; 8, water cooled copper coil; 9, desiccator; 10, saturated salt solution for maintaining constant humidity.

sample. For low temperature measurements the powder was placed on a metal rod, the lower end of which was held in a mixture of solid CO_2 ('dry ice') and iso-propyl alcohol (−78°C) or in liquid nitrogen (−196°C). A vertical electrical tube furnace was used for measurements above ambient. Above 200°C the fibre-optic reflectance probe was cooled by water passing through a copper coil wound tightly around it. It was not possible to use the probe above 500°C, since the proximity of the probe cooled the surface of the powdered sample, and the exiting cooling water was around 90°C. The recording of each spectrum took around 2 min, as a silicon detector was used. Measurements can, in principle, be achieved at higher temperatures using a fibre optic spectrophotometer equipped with a high-speed photo diode array or CCD detector and momentarily lowering the probe close to the powder surface.

Diffuse reflectance spectra at various humidities

Experiments were generally performed in air. However, since some monouranates hydrolyse in moist air to polyuranates, room temperature measurements were also carried out under various controlled humidities. These were achieved using saturated aqueous solutions of selected salts in contact with an excess of the solid phase at a controlled temperature in an enclosed space [13] A small vacuum desiccator was used as a chamber [Fig. 1(C)] and the measurements made at the relative humidities of 12% (maintained by saturated solution of $LiCl.H_2O$); 32% ($CaCl_2.6H_2O$); 52% ($Na_2Cr_2O_7.2H_2O$), and 76% ($CH_3COONa.3H_2O$). The atmosphere in the chamber was allowed to equilibrate with the required solution for 3–4 h before the powdered sample was quickly admitted. The probe was mounted vertically above the sample, through a rubber bung in the top of the desiccator, and spectra were recorded at suitable time intervals.

RESULTS

Effect of temperature

Figure 2 shows diffuse reflectance spectra recorded at −196°C for all the uranate compounds investigated. The main difference between the spectra of mono- and diuranates is that all diuranate species exhibit a strong absorbance between 420 and 490 nm (20 000–23 000 cm^{-1}), whereas the strongest absorbance region for monouranates lies below 440 nm (above 22 500 cm^{-1}). None of the uranates studied absorbed above 600 nm (below 16 600 cm^{-1}) at temperatures below ambient.

Increasing the temperature caused the expected broadening of the bands. Figure 3 shows in detail the change in the diffuse reflectance spectra of potassium mono- and diuranates as the temperature increases from that of boiling liquid nitrogen (−196°C) to around 500°C. Figure 4 shows the spectra of the lithium and sodium mono- and diuranates at these two temperature extremes and how significantly the component bands are narrowed upon cooling, so that their number and position can be established. The colour of all the uranates was predominantly pale yellow in liquid nitrogen, a deeper yellow to light salmon at room temperature, and orange when hot. The colours of the various uranates were systematised from their spectra using the trichromaticity colorimetry method [36–38].

Effect of humidity

Hydrolysis studies on the three monouranates (Li_2UO_4, Na_2UO_4 and K_2UO_4) showed that their tendency towards hydrolysis was $K_2UO_4 > Na_2UO_4 > Li_2UO_4$. The nature of the hydrolysis reaction of K_2UO_4 was dependent on humidity. Figure 5 shows the K_2UO_4 system as a function of time at various humidities. At humidities of 12 to 32% the spectral profiles were essentially similar and contained two isosbestic points, normally indicative of the presence of a two species equilibrium. However, the spectral

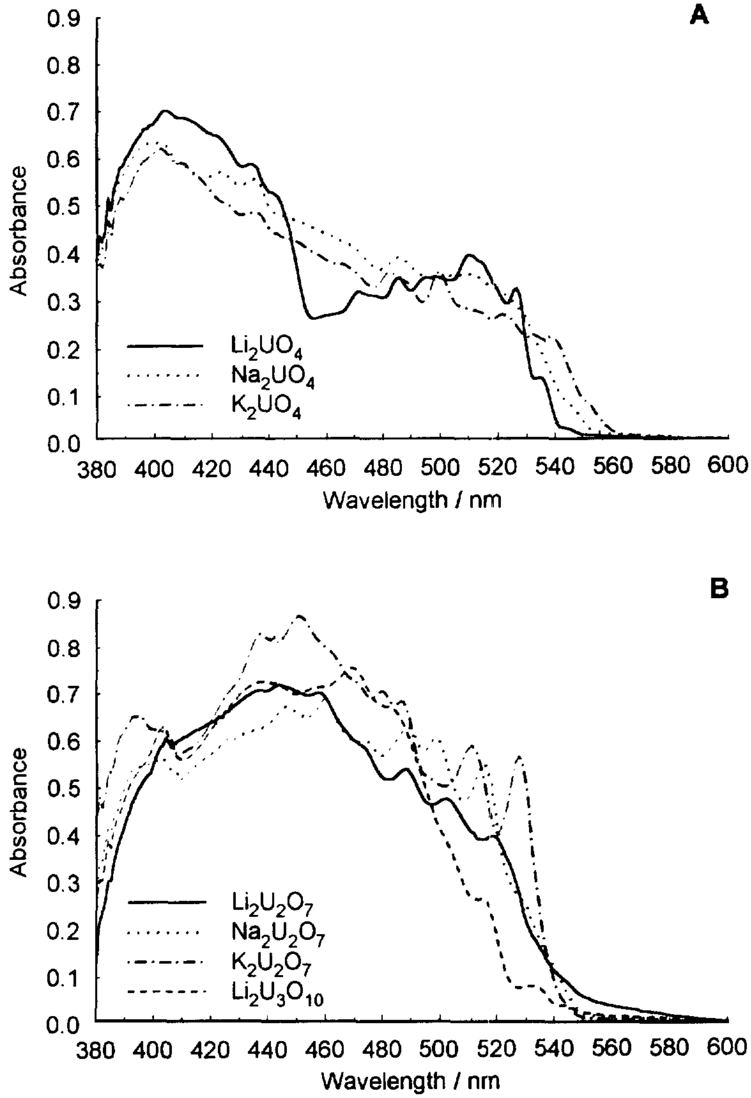

Fig. 2. Diffuse reflectance spectra recorded at −196°C of (A) alkali metal monouranates, M_2UO_4 (M = Li, Na, K), and (B) polyuranates, $M_2U_2O_7$ (M = Li, Na, K) and $Li_2U_3O_{10}$.

changes, and hence the reaction, proceeded faster at higher humidity. At 52% humidity a rapid initial increase in absorbance around 450 nm was accompanied by a decrease around 400 nm, followed by a general absorbance decrease over the wavelength range studied. A similar but faster process was observed at 76% humidity, but no isosbestic points were formed under these conditions.

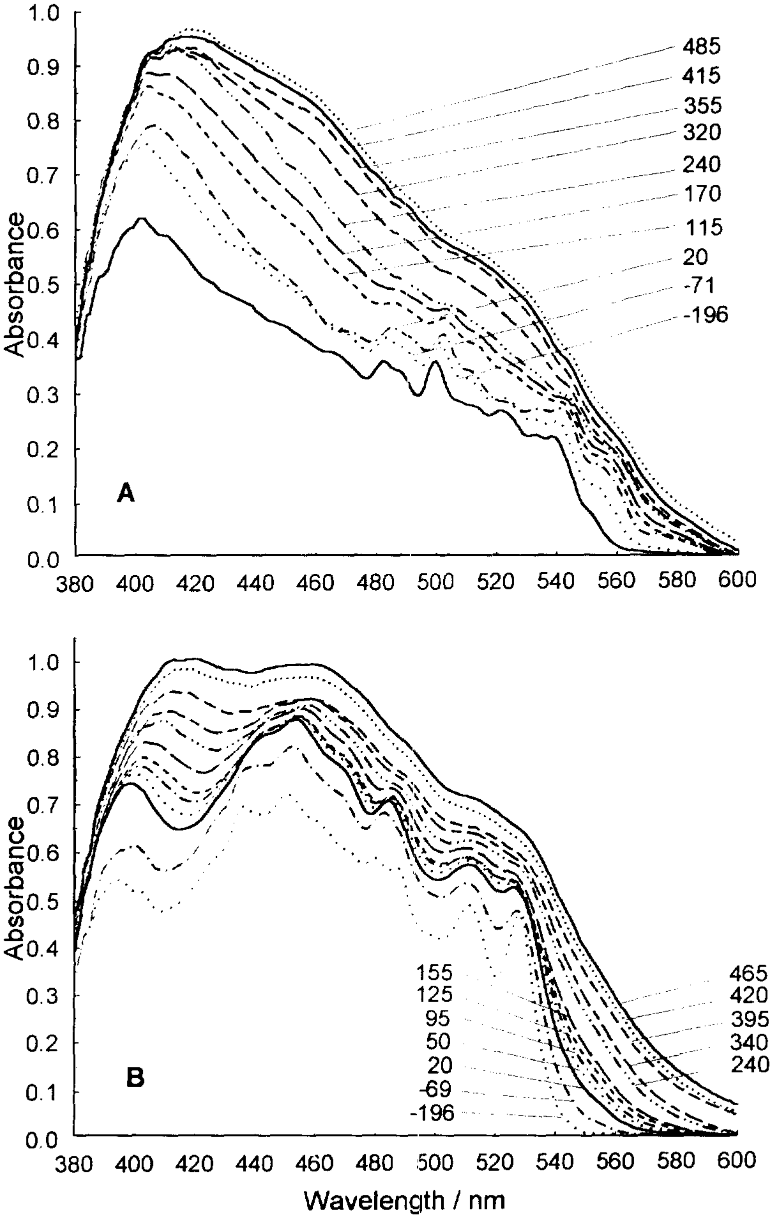

Fig. 3. The effect of temperature on the diffuse reflectance spectra of potassium uranates: (A) K_2UO_4 and (B) $K_2U_2O_7$. Numbers indicate degrees centigrade.

To resolve the dichotomy in the statements on the hydrolysis of sodium monouranate between Cordfunke and Loopstra [19] and Hoekstra [30] hydrolysis studies were carefully performed at different atmospheric moisture levels. Sodium monouranate was found to be much more stable than its

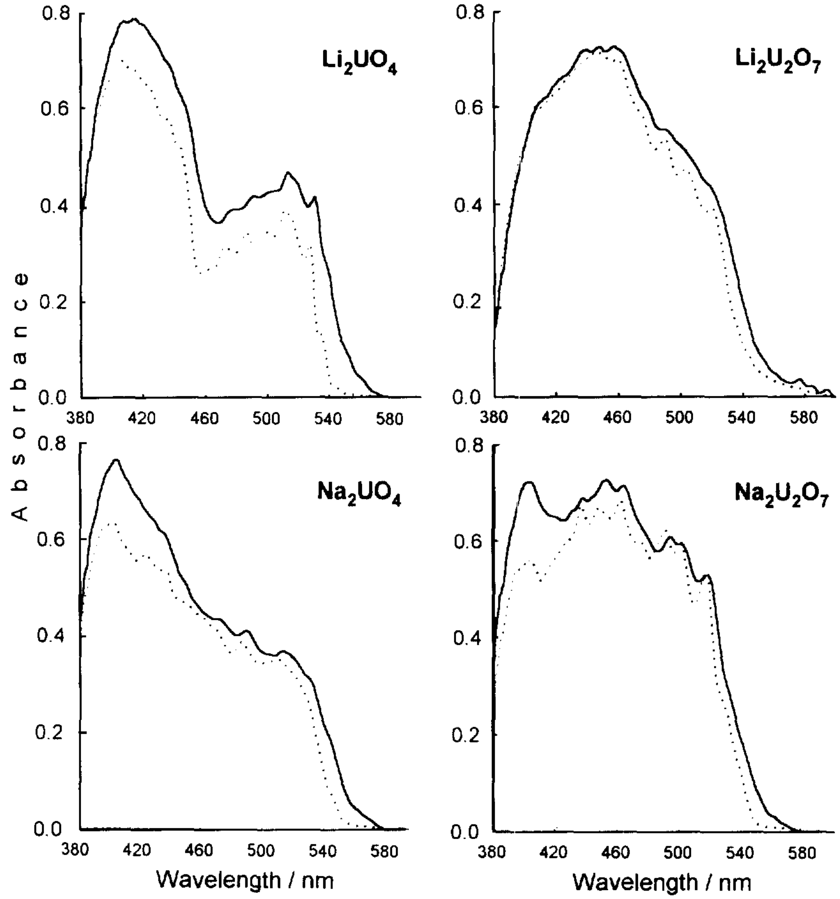

Fig. 4. The result of lowering temperature and consequent sharpening of the component bands in the diffuse reflectance spectra of lithium and sodium mono- and diuranates: upper lines, 20°C; lower lines, −196°C.

potassium analogue and changes in the spectra recorded under similar humidity conditions were significantly less. Both samples of Na_2UO_4 were investigated, the pure α form and the sample containing some of the β form. Pure α-Na_2UO_4 was more stable towards hydrolysis than the mixture. At a relative humidity of 52%, changes in the spectrum of the mixture became noticeable after 20 h exposure; the β-phase thus hydrolyses much the faster of the two forms. We therefore suggest that Cordfunke and Loopstra [19] had prepared the essentially non-hygroscopic α-phase, containing possibly only traces of the β-phase. Hoekstra [30], on the other hand, had a highly moisture sensitive form of sodium monouranate, which can now be identified as containing largely the β-phase, the different products resulting from the use of different temperatures in the preparation process.

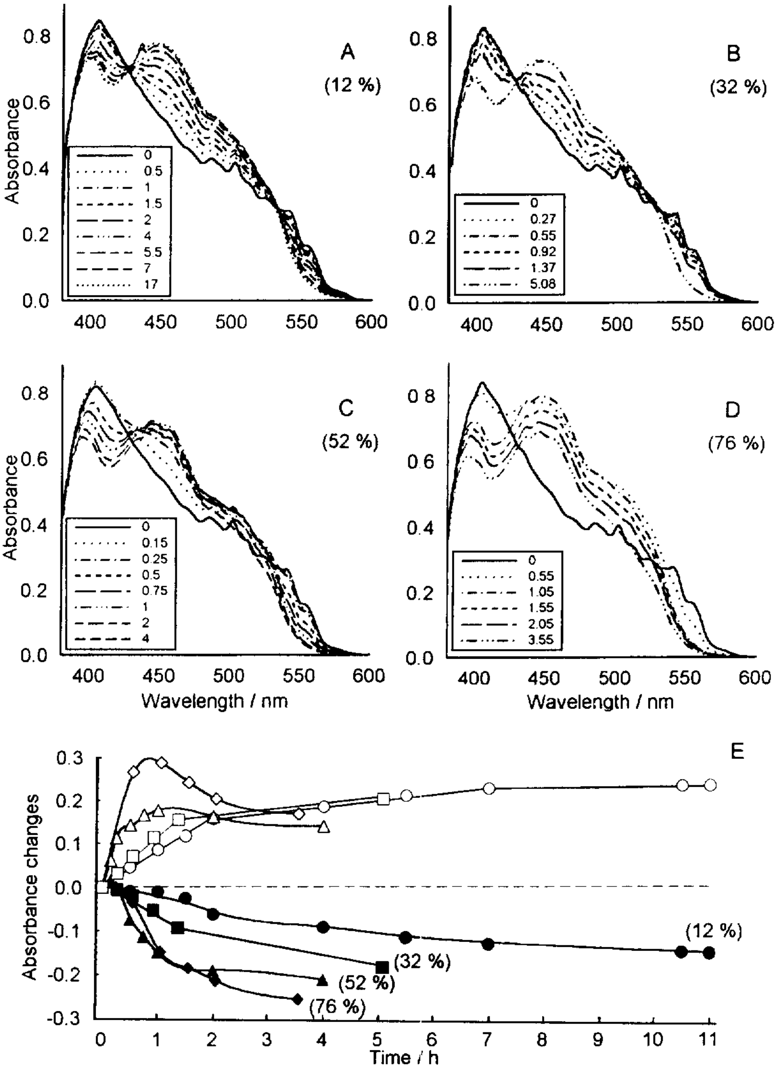

Fig. 5. (A)–(D): The effect on the diffuse reflectance spectrum of potassium monouranate upon exposure to air at different humidity levels. Relative humidity: (A), 12%; (B) 32%; (C) 52% and (D) 76%. Time of exposure (h) is given in the legend to each plot. (E): Changes in the absorbance in the spectra of K_2UO_4 exposed to the atmosphere at various humidity levels at 410 nm (solid symbols) and 455 nm (empty symbols). Values of corresponding humidities are shown in parentheses.

Lithium monouranate was essentially immune to hydrolysis, as no change could be observed in its diffuse reflectance spectrum after 16 h exposure to moist laboratory air at ambient temperature.

DISCUSSION

Absorption spectra of alkali metal uranates

The absorption spectra and colour of the uranate(VI) compounds arise from the charge transfer transitions from the bonding orbitals on oxygen to the non- or antibonding orbitals on uranium, and are therefore ligand-to-metal charge transfer transitions within the intrinsic uranate group. The diffuse reflectance spectra of alkali metal chromates, which can be viewed as analogues of the uranates, have been studied [39–41]. Above 350 nm they exhibit only two very broad bands, rather different from the complex structure observed in the spectra of the uranates (Fig. 2). There is, however, a major difference in the symmetries, viz, CrO_4^{2-} ion has four equal Cr–O bonds, placing it in the T_d point group, whereas the uranium atom has six coordinated oxygen atoms, but not regular octahedral symmetry. This is because it can be considered to be based on the uranyl group, with essentially two opposed doubly bonded oxygen atoms and four co-planar oxygen atoms shared with neighbouring uranium atoms. The monouranates studied here are usually regarded as having orthorhombic (Li_2UO_4, Na_2UO_4, K_2UO_4) or tetragonal (K_2UO_4) symmetry point groups, D_{2h} and D_{4h}, respectively. However, the symmetry of $K_2U_2O_7$ has been reported as low as monoclinic, (C_2), and that of K_2UO_4 as high as cubic [10, 19, 23, 30, 42, 43]. The site symmetry of the U(VI) ion responsible for the colour can be deduced from the reported data on crystal structure of the uranates.

The different absorption spectra profiles of the alkali metal uranates are compared in Fig. 2. For monouranates, the spectra recorded for the different alkali metals are quite similar, showing two clearly distinguishable regions below and above *ca.* 460 nm (22 000 cm^{-1}). The absorption profile in the low energy region is around 50–70% of that in the high energy region, and this difference is especially well pronounced in the spectrum of Li_2UO_4. The spectra of Na_2UO_4 and K_2UO_4 are similar but differ from that of Li_2UO_4. This is expected, since the α-form of sodium monouranate is structurally different from Li_2UO_4, and for all the structurally similar monouranates (lithium, β-sodium and potassium) [30] the distortion of U–O octahedra is greatest in Li_2UO_4.

The spectra of the diuranates, on the other hand, do not differ much from each other. Three regions can however be distinguished; viz, above 500 nm, between 410 and 500 nm, and below 410 nm. The absorption profiles in the middle region are slightly higher than those in the other two.

None of the uranates studied exhibited absorption above 625 nm. A weak absorption in this region has been reported for alkali earth metal uranates [44], particularly $MgUO_4$, $CaUO_4$ and $BaUO_4$, and this was associated with oxygen deficiency. The resulting presence of U(V), and possibly U(IV), gives rise to the absorption between 623 and 2500 nm, due to electronic transitions within the $5f$ orbitals of the uranium ions. Since we observed no absorbance in this region we can conclude that here no uranium in an oxidation state below +6 was present in the samples of alkali metal uranates.

Hydrolysis of alkali metal monouranates

The hydrolysis of a monouranate compound of general formula $M_2O.UO_3$ can be described by reaction (2):

$$x(M_2O.UO_3) + (x - 1)H_2O \rightarrow M_2O.xUO_3 + (2x - 2)MOH \qquad (2)$$

Previous studies by Pechurova *et al.* [32] showed that x was 1.94, 2.13, 3.80 and 3.63 for Li, Na, Rb and Cs, respectively. The tendency to form polynuclear species therefore increases with increasing radius of the alkali metal cation, and since the value for potassium was not obtained, it can be expected to be between 2 and 4. Thus, the end product could be potassium diuranate, but it is more likely that one or more higher uranates are additionally formed.

As essentially a standard, the spectrum of $Na_2U_2O_7$ was superimposed on the spectra measured during hydrolysis of Na_2UO_4 and was observed to pass through the recorded isosbestic points. Thus the product formed upon hydrolysis of sodium monouranate was the diuranate. However, this was not the case for the potassium salt. Here the final spectrum of the reaction (Fig. 5) more closely resembled that of lithium triuranate [Fig. 2(B)] and hence the polyuranate formed upon the hydrolysis of K_2UO_4 may be represented as $K_2O.xUO_3$, where $2 < x < 3$, but is closer to 3.

The spectra in Fig. 5 thus revealed that for K_2UO_4 at 12–32% relative humidity only one reaction product was formed, indicated by the presence of the isosbestic points in the complete set of spectra. However, at higher humidities (52–76%), several products were formed. Figure 5(E) illustrates how the absorbance was changed over time at different humidities. Data at 410 and 455 nm were chosen for comparison, because at these wavelengths the difference between mono- and polyuranates is easily identifiable. The absorbance is higher in the spectra of monouranates at 410 nm, but higher at 455 nm in the spectra of polyuranates. At low humidity (12–32%) at both wavelengths quite rapid changes (2–2.5 h) were initially exhibited, followed by a slowing down in the reaction rate as the system reached equilibrium (in *ca* 10–15 h). At high humidity (52–76%) no dramatic change occurred at 410 nm but at 455 nm an initial rapid increase in absorbance became more noticeable as the humidity was increased. This initial increase at 455 nm is associated with the formation of a polyuranate product, [reaction (2)], and the following decrease to further reaction of the polyuranate formed with the relatively large amount of the base KOH present, the second product of reaction (2) (and presumably forming a hydroxyuranyl complex). The high level of water content in the atmosphere makes this possible. Thus the initial changes in the spectra at 455 nm are associated with the formation of a polyuranate product, [reaction (2)], and occurred more rapidly with humidity increase.

Thermochromatism of alkali metal uranates

The colours of the various uranates have been conventionally characterised using D_{65} as the standard light source (imitating natural light) and 10° as the standard observer.

The chromaticity coordinates calculated on the basis of measured diffuse reflectance spectra at room temperature and in liquid nitrogen (−196°C) are presented in Table 2 and Fig. 6 shows the position of the colour parameters calculated using the CIELAB system.

The total colour difference between two chromatic points (ΔE^*) has been calculated [45] and the results for the alkali uranates at liquid nitrogen and room temperature are given in Table 3. The co-ordinates of the points on Fig. 6 correspond to the visual perception described by yellow to orange on heating.

Figure 7 and Tables 4 and 5 reveal for the first time the effect of large temperature changes upon chromaticity, exploring how the colour of

TABLE 2

Colorimetric Data for Alkali Metal Uranates at Room Temperature and −196°C

Compound	x	y	Y	L^*	a^*	b^*	u^*	v^*	h_{ab}
				Room temperature					
Li_2UO_4	0.4258	0.3932	69.0868	6.55	19.98	43.49	56.41	51.60	65.3
$Li_2U_2O_7$	0.4475	0.4150	66.264	85.13	19.08	56.54	60.63	63.83	71.4
Na_2UO_4	0.4223	0.3957	67.484	85.75	17.60	43.18	52.14	51.66	67.8
$Na_2U_2O_7$	0.4491	0.4150	69.123	86.56	19.90	57.81	62.79	65.17	71.0
K_2UO_4	0.4190	0.3924	68.501	86.26	17.78	41.47	51.65	49.94	66.8
$K_2U_2O_7$	0.4690	0.4209	64.793	84.38	23.90	65.00	72.28	69.21	69.8
				−196°C					
Li_2UO_4	0.3974	0.3919	80.172	91.76	10.49	38.29	38.46	49.05	74.7
$Li_2U_2O_7$	0.4368	0.4230	73.966	88.91	13.04	58.62	51.70	68.27	77.5
Na_2UO_4	0.4093	0.3992	77.450	90.53	12.11	43.26	43.51	53.95	74.4
$Na_2U_2O_7$	0.4375	0.4178	74.321	89.07	15.24	56.91	54.77	66.27	75.0
K_2UO_4	0.4012	0.3898	77.012	90.33	12.70	37.88	41.76	47.87	71.5
$K_2U_2O_7$	0.4533	0.4301	72.508	88.21	16.45	66.44	60.43	73.65	76.1

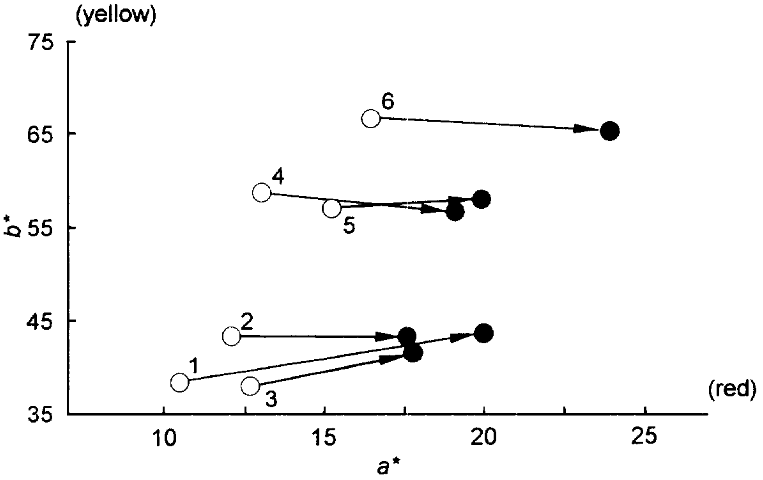

Fig. 6. Colours of alkali metal mono and diuranates at −196°C (empty symbols) and 20°C (solid symbols): 1,Li_2UO_4; 2,Na_2UO_4; 3,K_2UO_4; 4,$Li_2U_2O_7$; 5,$Na_2U_2O_7$; and 6,$K_2U_2O_7$.

TABLE 3
Colour Differences of Uranate Species at 20 and −196°C

	Li_2UO_4	Na_2UO_4	K_2UO_4	$Li_2U_2O_7$	$Na_2U_2O_7$	$K_2U_2O_7$
ΔE_{ab}*	12.01	7.28	7.43	7.42	5.37	8.50
ΔE_{uv}*	18.86	10.13	10.89	10.67	8.48	13.22

potassium mono- and diuranates change with temperature change from −196°C to around 500°C. Figure 7(A) shows that for both materials the amount of red constituent increased as the temperature rose. For $K_2U_2O_7$, the change was essentially linear with temperature, while for K_2UO_4 a change occurred at around 200°C. Figure 7(B) similarly shows that the yellow constituent of $K_2U_2O_7$ now decreased linearly with temperature increase, and again the monouranate seemed to show some change at the same temperature. We provisionally associate this change with some structural rearrangement commencing in the monouranate at higher temperatures. Figure 7(C) summarises the total changes in the colours of potassium uranates and clearly shows the difference in thermochromatic behaviour of the mono- and diuranate species.

Figure 7(D) shows the dependence of the metric lightness (L*) for K_2UO_4 and $K_2U_2O_7$ on temperature. Again, this parameter was temperature dependent, but this time obeying a linear relationship over the 700° range studied for the monouranate, but only up to *ca* 400°C for the diuranate. Up to this latter temperature, the lines were essentially parallel.

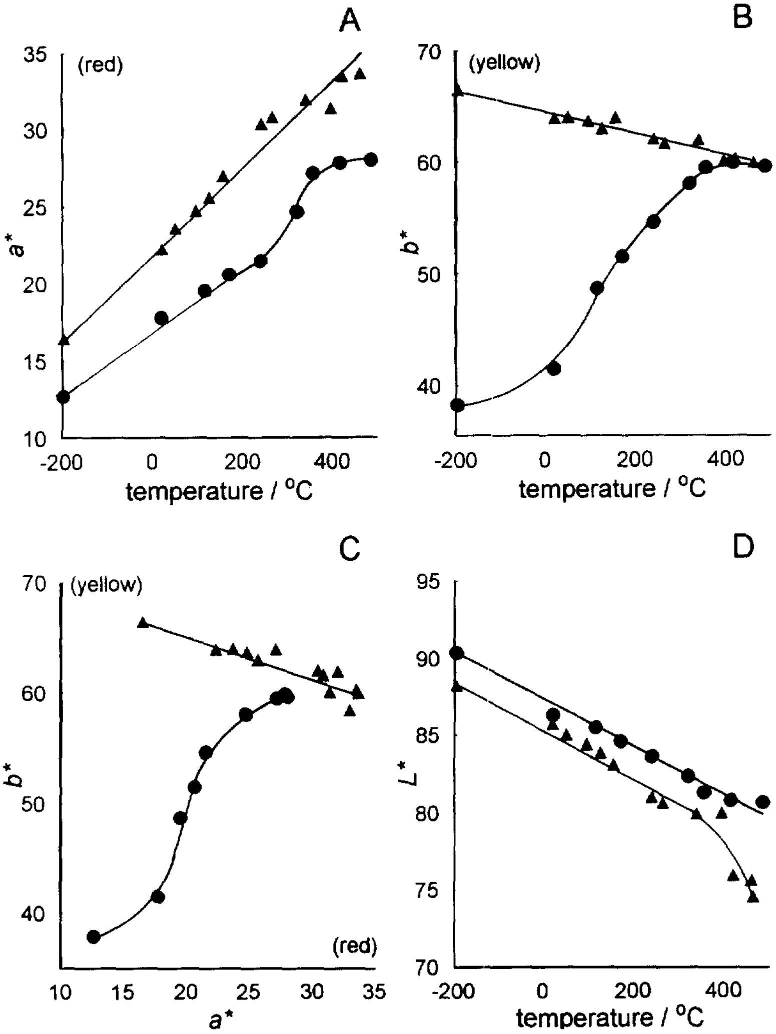

Fig. 7. The effect of temperature on colours of K_2UO_4 (●) and $K_2U_2O_7$ (▲): (A) and (B) changes in red and yellow constituents respectively; (C) total changes in the colours with temperature from −196°C to 485°C for K_2UO_4 or 465°C for $K_2U_2O_7$ (see Tables 4 and 5, respectively), and (D) the effect of temperature on the metric lightness.

No clear correlation between the effect of temperature on the colours of alkali metal uranates and their structural properties has to our knowledge been developed. Generally, temperature changes have a greater impact on the spectra of centrosymmetric species [46] than species having lower symmetry. Here, at all temperatures, the amount of the yellow component in the uranate colour increased as the basicity decreased, i.e. from mono- to polyuranates, which also reflects an increase in uranium content. We can

TABLE 4
Chromaticity Co-ordinates of Potassium Monouranate at Various Temperatures

Temperature (°C)	x	y	Y	L^*	a^*	b^*	u^*	v^*	h_{ab}
−196	0.4012	0.3898	77.012	90.33	12.70	37.88	41.76	47.87	71.5
25	0.4190	0.3924	68.501	86.26	17.78	41.47	51.65	49.94	66.8
115	0.4350	0.4024	66.893	85.45	19.50	48.65	57.93	56.61	68.2
170	0.4425	0.4059	65.116	84.54	20.60	51.44	60.97	58.74	68.2
240	0.4502	0.4100	63.237	83.57	21.46	54.55	63.67	61.04	68.53
320	0.4624	0.4116	60.874	82.31	24.63	57.94	70.43	62.73	67.0
355	0.4703	0.4109	58.904	81.24	27.12	59.37	75.23	62.87	65.4
415	0.4727	0.4108	57.991	80.73	27.78	59.79	76.49	62.85	65.1
485	0.4727	0.4102	57.733	80.59	27.94	59.48	76.62	62.51	64.8

TABLE 5
Chromaticity Co-ordinates of Potassium Diuranate at Various Temperatures

Temperature (°C)	x	y	Y	L^*	a^*	b^*	u^*	v^*	h_{ab}
−196	0.4543	0.4301	72.508	88.21	16.45	66.44	60.43	73.65	76.1
20	0.4631	0.4209	67.357	85.68	22.25	63.90	69.18	69.29	70.8
50	0.4663	0.4196	65.960	84.98	23.63	63.94	71.51	68.71	69.7
95	0.4684	0.4181	64.845	84.40	24.75	63.64	73.26	67.97	68.7
125	0.4695	0.4164	63.763	83.84	25.58	62.94	74.37	67.01	67.9
155	0.4743	0.4161	62.314	83.08	27.00	63.88	77.12	67.07	67.1
240	0.4800	0.4102	58.410	80.97	30.32	61.97	81.95	63.96	63.9
265	0.4806	0.4092	57.745	80.60	30.76	61.53	82.51	63.37	63.4
340	0.4841	0.4085	56.447	79.87	31.90	61.88	84.57	63.05	62.7
395	0.4802	0.4068	56.587	79.95	31.31	60.00	82.76	61.81	62.4
420	0.4906	0.4057	49.640	75.85	33.43	60.20	85.86	59.80	61.0
460	0.4872	0.4041	49.123	75.53	32.87	58.32	84.04	58.45	60.6
465	0.4927	0.4054	47.463	74.48	33.61	59.85	85.76	58.95	60.7

conclude from Table 3 that the colour of high symmetry species is more affected by temperature changes than species with lower symmetry, e.g. monoclinic $K_2U_2O_7$ and rhombohedral $Na_2U_2O_7$. However, further investigation is necessary before definite conclusions can be drawn concerning relationships between specific structural properties and the colour of closely related compounds.

CONCLUSIONS

The application of diffuse reflectance spectroscopy to an investigation of the hydrolysis of alkali metal uranates has shown that such measurements offer an interesting and useful tool for studying heterogeneous reactions between solid and gaseous phases. Further, the effect of temperature upon the stability or decomposition of coloured compounds may be easily followed using this technique and a suitable optical fibre probe. Since diffuse reflectance measurements have rarely previously been made above 130°C, this approach opens up a rapid and simple way to go beyond just observing colour changes in solids at elevated temperatures (decomposition, configurational changes, chromaticity, etc.), and now we can identify the reactions and mechanisms occurring, and the reaction rates, from the recorded diffuse reflectance spectra.

This study of uranates, while not currently pigments appealing to the general public, has resolved some long-standing discrepancies in the literature and opened a new way to extend thermochromaticity studies, using one of the oldest thermochromic groups of compounds.

This is the first time that the effect of temperature upon thermochromaticity has been investigated. It has been shown here that over a 700° range, when no physical (structural) change or chemical reaction is taking place, there is an essentially linear relationship between chromaticity coordinates and temperature. Further, when a reaction commences, this may be identified by a change in slope in such plots. Thus, in future, these features could be used to establish the thermal stability of compounds or mixtures, and perhaps more importantly, with thermally stable materials, to extend these relationships to higher (or lower) temperatures and *predict* the colours of thermochromic materials outside the experimentally measurable range.

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