Optical properties and colorimetry of gelatine gels prepared in different saline solutions

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Gelatine gels were prepared by gelation in solutions of transition metal chlorides. The properties of the resulting gels depend on the salt type and concentration. SDT values for the gelatine gels were correlated to the solutions’ concentrations. The gelatine gels exhibited significant improvement in their thermal stability. FTIR spectroscopy indicated a loss in the helical structure of the gels.

Gelatine has been widely used in many multidisciplinary research fields due to its biocompatibility. Using saline solutions in the gelation of gelatine allows for new properties to be incorporated into the prepared gels. This study examined the optical and colour properties of gelatine gels prepared in saline solutions, containing three different metal chlorides (NiCl₂·6H₂O, CoCl₂·6H₂O, and CrCl₃·6H₂O) with concentrations of up to 50%, to prepare three groups of gels. FTIR spectroscopy indicated a loss in the helical structure of the metal-containing gelatine gels, and a shift in the amide bands towards lower wavenumbers. From the thermogravimetric analysis (TGA), the starting degradation temperatures (SDTs) of the prepared gelatine gels were found to be correlated to the concentration of the gelling solutions. All SDTs were above 250 °C, making these gels suitable for standing temperatures beyond the daily range. UV–vis spectroscopy showed that d-d transitions were responsible for the colour properties of the metal-containing gelatine gels. It is concluded that the studied properties and the measured parameters were found to depend on both salt type and concentration. With the current findings, the prepared gels can be used as optical thermometers, colour-selective corner cube retroreflectors, laser components, and coatings for OLEDs.

Introduction

Gelatine is a polypeptide biopolymer that consists of proteins and peptides resulting from the partial reduction of protein during the hydrolysis process of collagen. Gelatine is soluble in hot water and most polar solvents. At room temperature, gelatine is a translucent, colourless brittle material that has an α-helical structure. However, some of gelatine’s physical properties, mainly its elastic properties, are highly sensitive to temperature variations [1,2]. The presence of different functional groups in gelatine’s structure, such as carboxyl and amino groups, provides gelatine the unique ability to complex with other materials [3,4]. To date, scientists have managed to alter many gelatine properties by...
adding other biomolecules and metal salts for different purposes [5,6]. Because of its biocompatibility, non-toxicity and low cost, gelatine has been used in many industries for various applications, including the food, pharmaceutical and medical industries [7–9]. The production of a non (or low)-degradable gelatine that can withstand temperature variations and ultraviolet radiation is desirable for widening the applications of gelatine to other medical and industrial fields, including those pertaining to photography, protective media, optical coatings, edible optics, eye-contact lenses, ocular tissue engineering, colour controllers and lacquered gelatine; one sample application is Wratten filters, which enable the selective transmission of certain wavelengths [1,10–13]. Such gels can also be used as filters for colour-selective corner cube retroreflectors and white OLEDs [11,14,15].

For the application of gelatine in the field of optics, it is essential to study gelatine’s optical and colour properties. The physical gelation of gelatine in saline solutions using different metal chlorides has been studied from the perspective of changes in the triple helical structure, changes in gelling temperature and the rheological and elastic properties of gelatine gels [1,2,16,17]. It is believed that the strength of gelatine gels decreases with the addition of chloride salts, while the gelling temperature increases with salt concentrations [1].

The current study is aiming to examine the improvements in the optical and colour properties of gelatine gels prepared by gelation in solutions containing different transition metal salts with different concentrations. The metal salts used in this work were nickel (II) chloride hexahydrate (NiCl₂·6H₂O, green), cobalt (II) chloride hexahydrate (CoCl₂·6H₂O, purple) and chromium (III) chloride hexahydrate (CrCl₃·6H₂O, dark green). These salts were chosen for their strong colour effects and ease of solubility in distilled water near room temperature [18,19]. Moreover, the metal chlorides used in this work are multivalent salts that contain additional counterions that may increase the crosslinking effect [7,20,21].

Although small amounts of these metal salts are considered harmless, caution should be taken in their use in applications that involve direct inhalation or ingestion. Cobalt plays a biologically essential role as a metal constituent of vitamin B12; however, excessive exposure has been shown to induce various adverse health effects [22]. Although Ni is considered an essential element in microorganisms, plants, and animals and is a constituent of enzymes and proteins, excessive Ni affects the photosynthetic functions of higher plants, causes acute and chronic diseases in humans and reduces soil fertility [23,24]. Little information has been reported on the toxicity of trivalent Cr. Available data show little or no toxicity associated with Cr(III) at levels reported on a per kg basis [25]. Cr(III) is also used as a nutrient supplement [26]. Independent studies should be conducted to determine the toxicity of the gelatine gels used in this research based on the levels of the metal salts present in the materials.

Herein, the thermal properties and degradation of the prepared samples are discussed in the TGA section in terms of the thermodynamic parameters. The macrostructure of gelatine gels is discussed in the Fourier transform infrared (FTIR) spectroscopy section in terms of the vibrational modes. Finally, discussions of the optical and colour properties are provided in the UV–visible spectroscopy and colour parameters sections, respectively.

Experimental

Materials

The gelatine used in this research is a type B food-grade powder (average MW 45000, bloom no. 175) supplied by E. Merck (Darmstadt, Germany). The gelatine’s maximum limit of ash impurity was 2.0%, and its grain size was less than 800 µm. Type B gelatine usually has an isoelectric point (IEP) between 4.8 and 5.4 [27]. Hydrated NiCl₂·6H₂O, CoCl₂·6H₂O and CrCl₃·6H₂O of 99.9% purity were supplied by Strem Chemicals Inc. (Newburyport, MA, USA). Samples were classified into three groups, each corresponding to one salt type. The salts were added in different weight concentrations with the help of a micro-analytical balance (Sartorius). The salt concentrations in the gelling solutions were 5%, 10%, 15%, 20%, 30% and 50% (see Table 1). The gelation process was performed for all samples under the same conditions as follows: Weighted amounts of gelatine and salts were dissolved separately in 100 mL of double-distilled water. The solutions were sterilized using an HL-320 tabletop autoclave at 121 °C for 15 min. The pressure inside the autoclave was then released, and the containers of the solutions were removed. Gelatine solutions were then mixed with the salt solutions of the corresponding weight percentage. The mixtures were further sterilized in a 65 °C water bath for 15 min until the gelatine and salt had thoroughly dissolved. The resulting solutions were poured into glass dishes with an area of 25 cm² and stored for a few hours at 4 °C. The dishes were then incubated for 30 to 45 min at 37 °C until a fine coating of thickness ~1 mm was formed.

Methodology

Thermal stability was investigated for the prepared gelatine gels using a computerized thermogravimetric analysis (TGA) instrument (TA-50) manufactured by Shimadzu Corporation (Kyoto, Japan). TGA measurements were performed in a nitrogen atmosphere under a flow rate of 0.5 mL/sec. A heating rate of 10 K/min was used for all samples over the temperature range from room temperature (~35 °C) to 600 °C. Fourier transform infrared (FTIR) spectra were measured for the prepared gelatine gels using a Shimadzu FTIR-8400S spectrophotometer (Shimadzu Corporation, Tokyo, Japan) over the wavenumber range 400 to 4000 cm⁻¹ (wavelength 2.5 to 25 µm). UV–visible absorption and transmission spectra were obtained for the prepared gelatine gels using a Perkin-Elmer 4-B spectrophotometer (Perkin-Elmer, Waltham, MA, USA) over the wavelength range of 200 to 800 nm.

Results and discussion

Thermogravimetric analysis (TGA)

Fig. 1 shows the TGA curves and their derivative curves (Dr-TGA) for all gelatine gels. The TGA curves of all gelatine gels exhibit three steps of degradation. The first step in the TGA curve represents a steep degradation phase from room temperature to T ~ 160 °C. During this phase, pure gelatine loses approximately 14.5% of its mass due to the evaporation of residual water absorbed from the atmosphere, which contributes significantly to the weight of gelatine. The second step of the TGA curve represents a shallow phase that starts from T ~ 160 °C and extends to ~240 °C (~241.6 °C for pure gelatine gels). This phase is characterized by a negligible loss in mass, which indicates negligible or no disintegration. It is worth mentioning that the upper temperature limit for that phase is far beyond the daily temperature range. The third degradation step is the steepest among the three phases, which starts at 245 °C and represents the main decomposition regime. This degradation phase is mainly associated with the disintegration and partial breaking of intermolecular structure due to endothermic hydrolysis and oxidation reactions [28]. Exothermic reactions occur after the pyrolysis of the derived collagen, leading to a mass loss of 85% at the end of the final degradation step. The remaining mass at 700 °C (973 K) was approximately 0.063% of the
original, most of which was ash formed by carbon residues. The remaining mass of the gels in the saline solutions was approximately 0.030% of the original mass.

Fig. 1 (a) shows that the starting decomposition temperature (SDT) for the main degradation phase increased with salt concentration, indicating an improvement in thermal stability. The DTG curves in Fig. 1 (b) show that the rate of decomposition during the main degradation phase for the Gel-Co gelatine gels increased with salt concentration. Moreover, Gel-Co20, Gel-Ni5 and Gel-Cr10 exhibited the maximum decomposition rate during their main degradation phase compared with the other concentrations in their corresponding groups. The percentage mass loss and the starting decomposition temperature for all gelatine gels are presented in Table 2.

The thermodynamic parameters of the gelatine gels were examined by employing the Coats–Redfern equation [29]:

\[
\ln \frac{-\ln(1 - x)}{T^2} = \frac{E^\theta}{RT} + \ln \frac{AR}{hE^\theta} \left[ 1 - \frac{2RT}{E^\theta} \right],
\]

where \(A\) is a pre-exponential constant, \(\theta\) is the heating rate, \(R\) is the universal gas constant (8.3145 J K \(^{-1}\) mol \(^{-1}\)), and \(x\) is the fractional decomposition at temperature \(T\) [29,30]. The relation in Eq. (1) was plotted for all the gelatine gels as shown in Fig. 2. The Coats–Redfern equation was fitted by a straight line to find parameter \(A\). Thermodynamic parameters such as the activation energy (\(E^\theta\)), enthalpy (\(\Delta H^\theta\)), entropy (\(\Delta S^\theta\)) and Gibbs free energy (\(\Delta G^\theta\)) were calculated based on the laws of thermodynamics as follows:

\[
\Delta H^\theta = E^\theta - RT,
\]

\[
\Delta S^\theta = 2.303 \frac{\Delta H^\theta}{R}\ln\frac{A}{kT},
\]

\[
\Delta G^\theta = \Delta H^\theta - T\Delta S^\theta,
\]

where \(k\) is Boltzmann’s constant and \(h\) is Planck’s constant. The Coats–Redfern relation for pure gelatine is shown in Fig. 2 (a). The calculated thermodynamic parameters for pure gelatine during the first degradation phase are \(E^\theta \sim 26.340\) kJ/mole, \(\Delta H^\theta \sim 23.430\) kJ/mole, \(\Delta S^\theta \sim -231.459\) J/mole and \(\Delta G^\theta \sim 104.440\) kJ/mole, whereas for the main degradation phase, \(E^\theta \sim 81.222\) kJ/mole, \(\Delta H^\theta \sim 76.250\) kJ/mole, \(\Delta S^\theta \sim -143.265\) J/mole and \(\Delta G^\theta \sim 161.922\) kJ/mole. The parameter values for all the gelatine gels are presented in Table 2.

A negative entropy value is a measure of orderliness. Small values of the thermodynamic activation parameters for the first degradation phase relative to those for the main degradation phase indicate relatively lower thermal motion, higher order and a more stable structure for materials heated to temperatures of up to \(\sim250\) °C.

**Fourier transform infrared (FTIR) spectroscopy**

An interaction between electromagnetic radiation and a molecule inside a material can only occur if there is a moving electrical charge associated with the molecule. Such movement is always the case when the molecule has either a variable or an inducible dipole moment (IR-active). In molecules with oscillations symmetric to the centre of symmetry, no changes in the dipole moment occur (IR-inactive). However, such “forbidden” vibrations are often Raman-active. In the case of polyatomic molecules, the fundamental vibrations are superimposed. Accordingly, a series of absorption bands that must be interpreted arises.

Fig. 3 presents the FTIR spectra of pure gelatine and the gelatine gels Gel-Co30, Gel-Ni30 and Gel-Cr30. The FTIR spectrum for pure gelatine in Fig. 3 consists of a broad amide I band at 3577 cm \(^{-1}\), a C=O stretching band in the amide I band at 1693 cm \(^{-1}\), an NH bending band at 1575 cm \(^{-1}\) and a CH2 bending band at 1575 cm \(^{-1}\) in the amide II band and an amide III NH bending band and a C=O stretching band at 1268 cm \(^{-1}\) and 1096 cm \(^{-1}\), respectively [31]. It is believed that the triple helical structure content of gelatine is closely related to the mechanical and physical properties of gelatine gels [32]. During the gelation process, the polymer structure changes from random separate coils to helical chains cross-linked by flexible peptide chains. The main interaction mechanisms involved in the conformations of gelatine chains are hydrogen bonds, hydrophobic effects and electrostatic interactions [1]. However, due to the large ionic strength of saline solutions, the addition of salt will cause a decrease in the electrostatic interactions due to electrostatic shielding, leaving the hydrogen bond mechanism as the main noncovalent source of stability for the helix structure. Moreover, the excess amount of multivalent counter ions in polyelectrolyte solutions will increase the probability of crosslinking or complexation between the multivalent counter ions and polyelectrolyte solution [7,21]. The FTIR spectra in Fig. 3 shows significant changes in the relative intensities and positions of the main bands, which depended on the type of salt. The transmittance relative intensities were measured for each spectrum relative to the baseline within the same spectrum. The baseline was considered the horizontal line that passes through the maximum point of the spectrum; this point was found to be approximately the same for all spectra at a transmittance value of \(\sim98.5\). The decrease in the relative intensities of the amide I, II and III bands for the metal-containing gelatine gels indicates an increase in disorder, which is associated with loss of the helix structure [33]. The intensity of the amide III band has been associated with the triple helical structure of the collagen-like content of the partly regenerated collagen, and a lower relative intensity of that band indicates gelatine gels host fewer intermolecular interactions [31]. The broader amide A band observed in the FTIR spectrum of the Gel-Co30 gelatine gel indicates a higher degree of molecular order, suggesting that gelatine gels of the Gel-Co group may have contained a significant number of intermolecular crosslinks of covalent bonds that survived the gelation process. Additionally, the inset in Fig. 3 shows a shift in the positions of the amide I C=O stretching band and the amide II NH bending band towards lower wavenumbers, which is dependent on the type of saline solution. These changes confirm the modification of the helical structure of gelatine, which is sensitive to experimental conditions such as temperature variations, the type of solvent used and ionic strength [2,17,34]. The degradation of the triple helix structure associated with the collagen-like content of the partly regenerated collagen during the gelling process was found to decrease the Bloom index.

### Table 1

| Sample group | 5% | 10% | 15% | 20% | 30% | 40% | 50% |
|--------------|----|-----|-----|-----|-----|-----|-----|
| Gelatine + CoCl₂ | Gel-Co5 | Gel-Co10 | Gel-Co15 | Gel-Co20 | Gel-Co30 | Gel-Co40 | Gel-Co50 |
| Gelatine + NiCl₂ | Gel-Ni5 | Gel-Ni10 | Gel-Ni15 | Gel-Ni20 | Gel-Ni30 | Gel-Ni40 | Gel-Ni50 |
| Gelatine + CrCl₃ | Gel-Cr5 | Gel-Cr10 | Gel-Cr15 | Gel-Cr20 | Gel-Cr30 | Gel-Cr40 | Gel-Cr50 |

The codes used in this research for the gel samples and their corresponding salt type and concentration according to the weight percentages.

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Fig. 1. TGA results and the corresponding differential curves for all gel groups; Gel-Co, Gel-Ni and Gel-Cr.
hence decreasing the gel strength [32,35]. Moreover, the shift of the amide I C=O and amide II NH bands to lower wavenumbers for the metal-containing gelatine gels implies a decrease in their gel strength when explained in terms of the local oscillator approach, in which an intermolecular bond can be approximated as a spring characterized by a force constant determining its length of absorbed light will be. If the energy of the number of conjugated double bonds is, the longer the wavelength of a molecule, its structure and its colour. The larger the number of conjugated double bonds is, the longer the wavelength of absorbed light will be. If the energy of π-to-π* transitions lies within the range of visible light, the colour of the molecule is complementary to that of the absorbed light. For the Gel-Co group of gels, as shown in Fig. 4 (a), two bands appeared in the visible parts of each spectrum. The peaks of the bands were centred around wavelengths 530 and 635 nm, which correspond to the transitions $^4A_{2g}$ – $^4T_{lg}$ and $^4I_{lg}[P] – ^4I_{lg}$ of the Co$^{2+}$ ion, respectively. The spectra of the Gel-Ni group of gels shown in Fig. 5 (a) indicate two main peaks characteristic of the hexaquo ion $[Ni(H_2O)_6]^{2+}$. The first peak is centred at approximately 400 nm and was assigned to the $^4A_{2g} – ^4T_{lg}$ transition, whereas the second peak is a broad one centred at approximately 722 nm and was assigned to the $^4T_{lg} – ^4I_{lg}$ transition. For the Gel-Cr group of gels, as shown in Fig. 6 (a), the transitions were due to complex ions consisting of the hexaquo ion $[Cr(H_2O)_6]^{3+}$ mixed with the aquo ions $[Cr(H_2O)_5Cl]^+$ and $[Cr(H_2O)_6Cl_2]^+$. The spectra were

### Table 2

The percentage mass loss, the starting decomposition temperatures (SDTs) and the thermodynamic parameters (activation energy $E^*$, entropy $\Delta S^*$, enthalpy $\Delta H^*$ and Gibbs free energy $\Delta G^*$) for the gels under study.

| Sample     | Temperature (K) | Mass loss | SDT °C | Thermodynamical parameters |
|------------|-----------------|-----------|--------|-----------------------------|
|            | Start | End  | %  | $E^*$ (kJ/mole) | $\Delta S^*$ (J/K/mole) | $\Delta H^*$ (kJ/mole) | $\Delta G^*$ (kJ/mole) |
| Gel-Co5    | 300   | 435  | 13.8 | 20.970 | -268.893 | 17.914 | 116.732 |
| Gel-Co10   | 560   | 900  | 85.9 | 21.857 | -257.365 | 15.788 | 203.664 |
| Gel-Co15   | 300   | 435  | 13.6 | 27.662 | -257.991 | 24.607 | 119.418 |
| Gel-Co20   | 560   | 900  | 86.2 | 23.721 | -252.378 | 17.651 | 201.888 |
| Gel-Co30   | 300   | 435  | 15.7 | 16.795 | -277.098 | 13.740 | 115.573 |
| Gel-Co40   | 560   | 900  | 87.0 | 24.078 | -240.078 | 20.050 | 199.687 |
| Gel-Co50   | 300   | 435  | 13.1 | 19.437 | -272.230 | 16.382 | 114.426 |
| Gel-Co10   | 560   | 900  | 87.7 | 254.000 | -242.082 | 23.331 | 198.736 |
| Gel-Co20   | 300   | 435  | 9.3  | 24.750 | -263.498 | 21.695 | 118.531 |
| Gel-Co30   | 560   | 900  | 88.5 | 35.619 | -228.324 | 28.550 | 196.957 |
| Gel-Co40   | 300   | 435  | 11.1 | 22.518 | -266.701 | 19.463 | 117.476 |
| Gel-Co50   | 560   | 900  | 88.7 | 30.738 | -240.635 | 24.669 | 200.333 |
| Gel-Ni5    | 300   | 435  | 13.3 | 55.602 | -201.205 | 52.547 | 126.490 |
| Gel-Ni10   | 560   | 900  | 86.7 | 22.643 | -255.750 | 16.574 | 203.272 |
| Gel-Ni15   | 300   | 435  | 18.8 | 34.293 | -242.596 | 31.238 | 120.391 |
| Gel-Ni20   | 560   | 900  | 81.0 | 44.530 | -203.740 | 38.461 | 187.192 |
| Gel-Ni30   | 300   | 435  | 14.5 | 48.891 | -216.065 | 45.836 | 125.240 |
| Gel-Ni40   | 560   | 900  | 85.3 | 22.501 | -256.374 | 16.432 | 203.585 |
| Gel-Ni50   | 300   | 435  | 12.4 | 51.838 | -209.906 | 48.783 | 125.924 |
| Gel-Cr10   | 560   | 900  | 87.4 | 31.567 | -244.003 | 18.400 | 203.822 |
| Gel-Cr15   | 300   | 435  | 31.6 | 39.523 | -231.636 | 36.468 | 121.594 |
| Gel-Cr20   | 560   | 900  | 81.2 | 322.355 | -256.770 | 16.572 | 204.014 |
| Gel-Cr30   | 300   | 435  | 8.2  | 25.550 | -266.482 | 19.495 | 117.427 |
| Gel-Cr50   | 560   | 900  | 91.6 | 33.115 | -238.356 | 27.046 | 201.046 |
| Gel-Ni5    | 300   | 435  | 12.7 | 55.602 | -201.205 | 52.547 | 126.490 |
| Gel-Ni10   | 560   | 900  | 80.0 | 22.643 | -255.750 | 16.574 | 203.272 |
| Gel-Ni15   | 300   | 435  | 18.8 | 34.293 | -242.596 | 31.238 | 120.391 |
| Gel-Ni20   | 560   | 900  | 81.0 | 44.530 | -203.740 | 38.461 | 187.192 |
| Gel-Ni30   | 300   | 435  | 14.5 | 48.891 | -216.065 | 45.836 | 125.240 |
| Gel-Ni40   | 560   | 900  | 85.3 | 22.501 | -256.374 | 16.432 | 203.585 |
| Gel-Ni50   | 300   | 435  | 12.4 | 51.838 | -209.906 | 48.783 | 125.924 |
| Gel-Cr10   | 560   | 900  | 87.4 | 31.567 | -244.003 | 18.400 | 203.822 |
| Gel-Cr15   | 300   | 435  | 31.6 | 39.523 | -231.636 | 36.468 | 121.594 |
| Gel-Cr20   | 560   | 900  | 81.2 | 322.355 | -256.770 | 16.572 | 204.014 |
| Gel-Cr30   | 300   | 435  | 8.2  | 25.550 | -266.482 | 19.495 | 117.427 |
| Gel-Cr50   | 560   | 900  | 91.6 | 33.115 | -238.356 | 27.046 | 201.046 |
Fig. 2. The Coats–Redfern relation for gelatine prepared in pure aqueous solution (a) and gels prepared in CoCl₂ (b), NiCl₂ (c) and CrCl₃ (d) solutions.

Fig. 3. FTIR spectra of gelatine gel prepared in aqueous solution and the gels Gel-Co30, Gel-Ni30 and Gel-Cr30. The inset is a magnification of the amide I C=O stretching band and the amide II NH bending band that indicates changes in these bands depending on the type of solvent.
characterized by two main peaks centred at approximately 430 and 590 nm assigned to the transitions $^4T_{2g} \rightarrow ^4A_{2g}$ and $^4T_{1g} \rightarrow ^4A_{2g}$, respectively.

To raise an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), the energy of the absorbed photon must exactly match the energy difference between the two energy levels. The wavelength of the absorbed light can be calculated according to the formula $E = h\nu = \frac{hc}{\lambda}$, where $E$ is the energy of the absorbed light, $h$ is Planck’s constant, $c$ is the speed of light and $\lambda$ and $\nu$ are the frequency and wavelength of the electromagnetic wave, respectively.

The band gaps between the transition levels can be calculated from the Tauc plots, which plot $(zh\nu)^2$ versus $h\nu$. Here, $z$ is the absorption coefficient and is directly determined from the optical absorption data provided by the UV–vis spectrometer using the Urbach equation. The exponent $r$ used in the Tauc plots can assume four values: $r = 1/2$ for direct allowed transitions, $r = 3/2$ for direct forbidden transitions, $r = 2$ for indirect allowed transitions and $r = 3$ for indirect forbidden transitions. Only the allowed transitions were considered in this research; thus, the Tauc relations using $r = 1/2$ for direct transitions and $r = 2$ for indirect transitions were plotted as shown in Figs. 4–6 for the Gel-Co, Gel-Ni and Gel-Cr groups, respectively. The linear part of the curve is extrapolated to intersect with the $x$-axis at the band gap value.

For pure gelatine, the value of the direct allowed band gap is 5.217 eV. The values of the direct band gaps $E_d$ and the indirect band gaps $E_{in}$ for the gelatine gels are shown in Table 3.

Along the absorption coefficient curve and near the optical band edge, there is an exponential part called the Urbach tail. The exponential tail appears because of the existence of localized states that extend into the band gap. In the range of low photon energy, the spectral dependence of the absorption coefficient ($\alpha$) and photon energy ($E$) is given by the equation $\alpha = \alpha_0 \exp \left( \frac{E}{E_U} \right)$, where $\alpha_0$ is a constant and $E_U$ denotes the energy of the band tail. Taking the natural logarithm of the two sides of the equation, one can obtain a straight line representing the relation between $\ln(\alpha)$ and the incident photon energy ($E = h\nu$), as shown in Figs. 4–6, for the Gel-Co, Gel-Ni and Gel-Cr groups, respectively. The band tail energy, or Urbach energy ($E_U$), can be obtained from the slope of the straight line. The Urbach energy for pure gelatine was found to be 0.312 eV. The Urbach energies for the metal-containing gelatine gels are listed in Table 3.

**Colour parameters**

The method of trichromaticity colorimetry enables determination of the colour trajectory in the Commission Internationale de l’Eclairage (CIE) 1931 colour space, where each colour corresponds to the appropriate and unique point in that space whose positional parameters are related to the tristimulus values $X$, $Y$, and $Z$ [38]. The CIE standard colour system was defined by the International Commission on Illumination to establish a relationship...
between human colour perception and the physical causes of colour appeal using the colour space coordinates. The three basic values of the colour space coordinates X, Y and Z are called tristimulus values. Each colour can be identified by such a triplet consisting of the normalized tristimulus values x, y and z. Thus, the term tristimulus system is customary for the CIE standard system.

The tristimulus values for a colour can be calculated from the spectral reflectance values \( R(\lambda) \) using the following integrals over the visible wavelength range (380 to 780 nm):

\[
X = \frac{K}{N} \int_{380}^{780} R(\lambda) I(\lambda) \tilde{x}(\lambda) d\lambda
\]

\[
Y = \frac{K}{N} \int_{380}^{780} R(\lambda) I(\lambda) \tilde{y}(\lambda) d\lambda
\]

\[
Z = \frac{K}{N} \int_{380}^{780} R(\lambda) I(\lambda) \tilde{z}(\lambda) d\lambda
\]

where \( N = \int_{380}^{780} I(\lambda) \tilde{z}(\lambda) d\lambda \), \( K \) is a scaling factor (usually 100) and \( I(\lambda) \) is the spectral power distribution of the spectrometer lamp. \( \tilde{x}(\lambda) \), \( \tilde{y}(\lambda) \) and \( \tilde{z}(\lambda) \) are called the colour matching functions. The parameter Y is also a measure of the luminance of a colour.

The normalized tristimulus (chromaticity coordinates) values were calculated for the gelatine gels using the following equations:

\[
x = \frac{X}{X + Y + Z}
\]

\[
y = \frac{Y}{X + Y + Z}
\]

\[
z = \frac{Z}{X + Y + Z} = 1 - x - y
\]

Fig. 7 represents the CIE chromaticity coordinate of the studied gelatine gels with respect to a white D65 reference source. The colour of the gelatine gels can be varied by changing the salt type and concentration. For the Gel-Co group of samples, as shown in Fig. 7 (a), the colour of the gelatine gels changed from near the white point towards the purplish blue with increasing CoCl\(_2\) concentration. As shown in Fig. 7 (b), the increase in the NiCl\(_2\) concentration led to a change in the colour of the gelatine gels towards the yellow-green region, whereas the change in colour for the Gel-Cr group, as shown in Fig. 7 (c), was found to be towards the green as the CrCl\(_3\) concentration increased. The colours of the gelatine gels of the Gel-Co group were close to the Planckian locus, whereas the colours of the low-salt-concentration gelatine gels in the Gel-Ni and Gel-Cr groups were near the white region and possessed small colour gradients. The blackbody correlated colour temperature (CCT) can be calculated from the chromaticity coordi-
Hue (Hue) is another parameter perceived by people as a fundamental characteristic of colour. In colour theory, hue refers to the property according to which one distinguishes colour sensations, for example, red, yellow or green. A colour of the same hue can either vary in saturation, such as grey blue versus blue, or in brightness, for example pink versus red.

Chroma (C*) describes the relative colour effect relative to the reference white, i.e., relative to the brightest point of a colour space. The chroma is suitable as a measurement value for conical colour spaces, for example, where it can be measured from the top. These systems are useful in the printing industry. The colour parameters obtained for the gelatine gels are presented in Table 4.

The differences in brightness (ΔL'), red-green colour (ΔU') and yellow-blue (ΔV') colour were calculated with respect to the properties of the pure gelatine gel [40]. Table 4 shows that the gelatine gels of the Gel-Ni group became more greenish and more yellowish as the concentration of the gelling solution increased. Additionally, the chroma of all the gelatine gels tended to increase with concentration. Fig. 7 (d) and (e) show the change in brightness difference (ΔL') and CCT according to the concentrations of the gelation solution, respectively. For the Gel-Co and Gel-Cr groups, the brightness difference tended to decrease with increasing concentration, whereas the CCT value increased with concentration. For the Gel-Ni group, CCT tended to decrease with concentration.

Table 3
The values of the direct band gaps $E_d$, the indirect band gaps $E_i$, and the Urbach energies $E_U$.

| Sample    | $E_d$ (eV) | $E_i$ (eV) | $E_U$ (eV) |
|-----------|------------|------------|------------|
| Gel-Co5   | 4.876      | 2.825      | 0.828      |
| Gel-Co10  | 5.238      | 2.727      | 0.395      |
| Gel-Co15  | 4.415      | 4.084      | 0.510      |
| Gel-Co20  | 5.314      | 3.690      | 0.506      |
| Gel-Co30  | 4.772      | 3.623      | 0.084      |
| Gel-Co40  | 4.312      | 3.787      | 0.060      |
| Gel-Co50  | 4.136      | 3.814      | 0.069      |
| Gel-Ni5   | 4.675      | 3.591      | 0.609      |
| Gel-Ni10  | 4.447      | 3.572      | 0.636      |
| Gel-Ni15  | 4.112      | 3.510      | 0.791      |
| Gel-Ni20  | 4.076      | 3.527      | 0.641      |
| Gel-Ni30  | 4.271      | 3.434      | 0.291      |
| Gel-Ni40  | 3.985      | 3.304      | 0.321      |
| Gel-Ni50  | 4.203      | 4.015      | 0.712      |
| Gel-Cr5   | 4.198      | 3.677      | 1.189      |
| Gel-Cr10  | 3.986      | 2.370      | 1.527      |
| Gel-Cr15  | 4.803      | 3.866      | 0.157      |
| Gel-Cr20  | 3.534      | 2.465      | 1.085      |
| Gel-Cr30  | 4.613      | 2.316      | 0.132      |
| Gel-Cr40  | 3.537      | 3.194      | 0.131      |
| Gel-Cr50  | 3.455      | 3.182      | 0.101      |
Fig. 7. Commission Internationale de l’Eclairage (CIE) 1931 colour space for (a) Gel-Co group of gels, (b) Gel-Ni group of gels and (c) Gel-Cr group of gels. (d) and (c) The dependences of brightness difference ($D_L^*$) and CCT on solvent concentration, respectively.

Table 4
The difference in colour parameters (brightness $D_L'$, red-green $D_U'$, yellow-blue $D_V'$ and chroma $D_C'$) calculated with respect to those of the gelatine gel prepared in pure aqueous solution. The blackbody correlated colour temperature (CCT) in Kelvin and hue ($H_{hue}$) for the gels under study.

| Sample   | $D_L'$  | $D_U'$  | $D_V'$  | $H_{hue}$ | $D_C'$  | CCT (K) |
|----------|---------|---------|---------|-----------|---------|---------|
| Gel-Co5  | -15.123 | 7.051   | -13.958 | 159.996   | 15.638  | 6099.0  |
| Gel-Co10 | -15.748 | 11.781  | -24.526 | 51.630    | 27.209  | 8120.2  |
| Gel-Co15 | -35.061 | 9.291   | -49.747 | 78.025    | 50.607  | 15228.9 |
| Gel-Co20 | -68.285 | 27.708  | -46.854 | 53.392    | 54.434  | –       |
| Gel-Co30 | -81.151 | 13.132  | -85.334 | 80.785    | 54.434  | –       |
| Gel-Co40 | -93.383 | 1.570   | -31.011 | 88.576    | 31.050  | –       |
| Gel-Co50 | 9.000   | 0.739   | 3.183   | 91.350    | 3.268   | 5795.0  |
| Gel-Ni5  | -17.471 | -3.154  | 6.205   | 83.105    | 6.961   | 5739.0  |
| Gel-Ni10 | -17.602 | -4.266  | 9.882   | 81.308    | 10.764  | 5652.6  |
| Gel-Ni15 | -9.000  | -0.739  | 3.183   | 91.350    | 3.268   | 5795.0  |
| Gel-Ni20 | -7.967  | -6.915  | 18.207  | 78.690    | 19.476  | 5559.9  |
| Gel-Ni30 | -1.999  | -10.136 | 23.916  | 75.450    | 25.975  | 5558.4  |
| Gel-Ni40 | -8.278  | -8.268  | 22.476  | 77.870    | 41.400  | 5483.1  |
| Gel-Ni50 | -17.700 | -13.670 | 39.078  | 75.880    | 4.136   | 5152.8  |
| Gel-Cr5  | -15.676 | -4.199  | -1.104  | 72.472    | 4.341   | 6111.1  |
| Gel-Cr10 | -30.789 | -5.432  | -5.984  | 49.013    | 8.082   | 6417.5  |
| Gel-Cr15 | -6.262  | -13.356 | 1.631   | 45.804    | 13.455  | 6469.8  |
| Gel-Cr20 | -44.236 | -15.903 | 0.055   | 36.705    | 15.903  | 6816.0  |
| Gel-Cr30 | -88.847 | -12.018 | -3.361  | 34.913    | 12.480  | 7840.4  |
| Gel-Cr40 | -79.685 | -26.336 | 3.597   | 29.728    | 26.878  | 8686.2  |
| Gel-Cr50 | -97.132 | -1.872  | -10.441 | 35.016    | 10.607  | 8352.5  |
Conclusions

This research represents a study of the thermal, optical and col- orimetric properties of gelatine gels prepared in different saline solutions containing the transition metal salts NiCl₂, 6H₂O, CoCl₂.6H₂O and CrCl₃.6H₂O. The effect of salt concentration on the studied properties was considered, and the variables were compared within the same salt type for different concentrations and for the different salts, taking into account the properties of gelatine gels. A spectroscopic study utilizing FTIR was performed on the gelatine gels to investigate the nature of interactions between the salt ions and the gelatine functional groups. The results suggested the existence of crosslinking or complexation interactions either by direct linking of the ions to the gelatine bridge or by indirect effects on peptide folding by interacting with structurally linked water molecules. The results showed that the changes in the gelatine helical structure were highly sensitive to salt type and concentration. These changes had a direct effect on the structural and physical properties of the prepared gelatine gels. The results of FTIR and TGA indicated that the gel strength of the gelatine gels decreased due to the addition of chloride salts, whereas their thermal stability increased with salt concentration. UV–vis spectroscopy showed that the d-d transitions corresponding to the wavelengths in the visible region were responsible for the colour properties of the gelatine gels. The colours of the Gel-Co group were found to be near the Planckian locus region, and CCT steadily increased with CoCl₂ concentration. This sensitive dependence of the salt concentration on the CCT allows for these gels to be used as accurate optical thermometers (temperature sensors and transducers) in extreme temperature environments, such as the turbine inlet in jet engines, stationary gas turbine power plants and nuclear reactor plants. The gels of the Gel-Co group can also be used as filters for colour-selective corner cube retroreflectors, which can be applied in satellite communication, laser components and antennas. The colours of the Gel-Ni and Gel-Cr groups were found to be near the white region and possessed small colour gradients correlated to concentration. The gels of the Gel-Ni and Gel-Cr groups show promise for producing good-quality coatings and filters for white OLEDs. All studied physical properties and the calculated parameters were found to be highly sensitive to the salt concentrations.

Conflict of interest

The authors have declared no conflict of interest.

Compliance with Ethics Requirements

This article does not contain any studies with human or animal subjects.

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