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Corresponding Author: Dr. FRANCESCA CATERINA IZZO, PhD

Corresponding Author's Institution: Ca' Foscari University of Venice

First Author: FRANCESCA CATERINA IZZO, PhD

Order of Authors: FRANCESCA CATERINA IZZO, PhD; Valentina Vitale; Chiara Fabbro, PhD; Henk van Keulen

Abstract: We present a multi-analytical study on the formulation of commercial felt-tip pens, introduced in the second half of the 20th century and commonly used by modern and contemporary artists. These media of both drawing and writing have not yet been fully investigated, but the degradation processes they might undergo, such as fading, are well-known and rather apparent. Twelve water-based felt-tip pens were investigated by the joint use of complementary analytical techniques, such as Thin Layer Chromatography, Nuclear Magnetic Resonance, Fourier transformed Infrared spectroscopy, X-Ray Fluorescence spectrometry and Pyrolysis-Gas Chromatography/Mass Spectrometry.
The obtained results provided crucial, preliminary data for the identification of dyes, solvents and additives present in the inks' formulations. Numerous synthetic food colouring agents and pigments were identified, such as Acid yellow 23, Acid Red 18, Acid Blue 9, Pigment Blue 15. In addition, glycols, fatty acids, 2-phenoxyethanol, colophony, benzotriazole derivatives and other solvents and additives were detected in the manufactured inks.
Furthermore, the effects of photo-degradation on one emblematic ink sample were studied, highlighting in particular visual and aesthetical changes due to discolouration.
This study demonstrates a methodology based upon the use of an integrated analytical approach for the characterisation of commercial ink-based artistic media and their viable degradation patterns, which aims to develop suitable conservation treatments to assess modern and contemporary drawings and writings.

Cover Letter

Dear Editors and Guest Editor,

We present the paper titled “Multi-analytical investigation on felt-tip pen inks: formulation and preliminary photo-degradation study”.
Markers and felt-tip pens have been introduced in the second half of the 20th century and nowadays are commonly used for artistic purposes by contemporary artists. These drawing and writing media have not been fully investigated yet, but well-known and visible are the degradation processes they might undergo, e.g. fading.
In this study we focused on the composition of some of the most used modern felt-tip pens’ inks by Pentel (japan), Stabilo (Germany), Giotto (Italy) and Lyra (Italy). The application of different complementary techniques (such as TLC, Py-GC/MS, XRF, FTIR and NMR spectroscopies) was fundamental to investigate dyes, solvents and additives present in the commercial formulations which are usually covered by trade secret.
Furthermore, we study the effect of accelerated photo-degradation (induced by a solar lamp) on one emblematic ink sample, monitoring its behavior over time. Degradation, in particular fading and discolouration, was registered in a very short time of solar lamp exposure (24 hours), according to the variations of colorimetric parameters La* b* (CIE-LAB).
This research provides preliminary important data both for the identification of commercial ink-based artistic media and their possible degradation patterns, aiming to develop suitable conservation treatments to assess modern and contemporary drawings and writings.

We are confident that the article can contribute to the specific focus of this special Issue on Analytical methods to study modern and contemporary art.

Best wishes,

Francesca Caterina Izzo in the behalf of the authors

*Detailed Response to Reviewers

Dear Editor

Dear Reviewers

First of all, we would like to thank you for the comments you did on our article. We took into consideration your suggestions for improving the text, which is attached as revised manuscript.

A detailed response to your comments/corrections/suggestions is here presented:

Reviewer #1:

1- **The text of the article would benefit from proof-reading by a native English speaker**

The text was corrected by a British speaker.

2- **The dissertation-like structure of the paper is not clear since a large number of analytical approach were applied for the characterization and the ageing studies of the reference materials. The paper should be reorganized in order to make clear the advantages of each analytical procedure and enlighten the analytical results obtained for all the fresh and aged samples.**

We partially reorganized the structure and highlighted the advantages of each techniques.

3- A number of relevant Py-GC/MS studies on modern organic dyes , described in the literature, are not cited in the paper. Especially the studies presented by Russell et al. (The identification of synthetic organic pigments in modern paints and modern paintings using pyrolysis-gas chromatography-mass spectrometry Anal Bioanal Chem (2011) 400:1473-1491) and Ghelardi et al. (Py-GC/MS applied to the analysis of synthetic organic pigments: characterization and identification in paint samples, Anal Bioanal Chem (2015) 407:1415-1431) were obtained by the application of a similar pyrolysis apparatus as the one used in this study. These references should be included in the bibliography for the identification of the origin of the organic dyes in the analyzed samples.

The references were added in the text

4- 5- The use of TLC for the characterization of the aged dyes allows the identification of only a limited fraction of the degradation products, because the detection limit of TLC is relatively high, suitable for major components only. It is possible that the dyes that does not show any significative change during the ageing were characterized by the presence of degradation products in low amount, not detectable with the TLC system? The repeatability and reproducibility of the TLC system were tested?

The referee's comment underlying the detection limit of TLC is correct. Nevertheless, the identification of degradation products, which might indeed be present in low amounts, was not carried out through this technique. As stated in paragraph 2.3, the aged samples were analysed by spectro-colorimetric measurements, FTIR and NMR spectroscopies.

As far as the need to test reproducibility is concerned, we thank the referee for this comment, which is appropriate. Indeed, this issue was addressed and each TLC run was repeated several times to confirm the outcome. A sentence has been added in the text (paragraph 2.2) to specify it.

6- The NMR and FTIR spectra should be included in the supplementary material.

We thank the referee for this suggestion. We added the spectra in a separated supplementary information file, together with all the relevant comparisons and enlargements.

7- A summarizing table with features of NMR peaks and the IR absorption bands should be included in the paper.

A table summarizing the IR absorption bands has been included (Table 4).

For what concerns NMR, the full assignment has been done and reported for the red and yellow fractions of sample GBk (Figure 4). For all the other samples, the spectra have been added as supplementary material.

8- In the PY-GC/MS section the pyrolyzer model is 3030D

Yes, indeed the model in 3030D!

Reviewer #2:

1.This paper needs thorough editing of language + English

The text was corrected by a British speaker.

2. I understand from the cover letter that this paper is submitted to a Special Issue on Analytical methods to study modern and contemporary art, but it stays unclear to me how the study presented links with real art works. Did you identify commercial felt-tip pen inks in real art works? Based on this study, do you expect to be able to identify these inks in real art works? What problems would you expect?

Museum's collections include also artworks produced by using felt-tip pen, as it has come to light by our survey at Internationally Gallery of Modern Art Ca' Pesaro (Venice), now mentioned in the text (paragraph1). It was not possible to contact the authors of the drawings, therefore the selection of the investigated sample was based on the information given by an artistic collective.

3. I would like to see a more critical review of the analytical techniques used in this study. The following questions can be addressed: - Can you distinguish between the different inks with the techniques used in this study? -How do the techniques complement each other? - Which techniques are the most crucial in identifying the inks, or provide the most information? -How can the techniques be applied on samples of real artworks, in terms of sample size and sample preparation?

The issue regarding the identification of the commercial ink was evaluated, as it was possible for some brands identify specific compounds used as additives. A sentence has been added in the text (paragraph 4) to specify it. Nevertheless, the achievement of this information would be related to the artists' technique, while we would like to underline that the main target of this study is the knowledge of the composition for conservation purpose.

Comparison between the advantage of each technique was included in the conclusion.

The referee's questions regarding the application of the techniques on samples of real art works are understandable and comments concerning it have been included in the conclusion. Nevertheless, this study is an investigation on the composition of raw inks: this is the first step necessary to set a suitable extraction as pre-analytical sample treatment for the further studies on real art works.

Francesca C. Izzo on the behalf of the authors

***Highlights (for review)**

Highlights:

- the current research is among the first studies related to felt-tip pen inks used for artistic purposes.
- the study takes focuses on the chemical formulation of commercial inks from 12 felt-tip pens produced in Germany, Italy and Japan.
- furthermore, this study takes into consideration the effect of photo-degradation on one emblematic ink sample and its monitoring over time.

Multi-analytical investigation on felt-tip pen inks: formulation and preliminary photo-degradation study

Francesca Caterina Izzo[1*], Valentina Vitale[1], Chiara Fabbro[2], Henk Van Keulen[3]

1. Ca' Foscari University of Venice, Department of Environmental Sciences, Informatics and Statistics, Via Torino 155/b, Venice
2. Ca' Foscari University of Venice, Department of Molecular Sciences and Nanosystems, Via Torino 155/b, Venice
3. Cultural Heritage Agency of the Netherlands, Hobbemastraat 22, 1071 ZC Amsterdam

***Corresponding author**: fra.izzo@unive.it 0039-0412346730 (T), 0039-0412346729 (F)

Abstract

We present a multi-analytical study on the formulation of commercial felt-tip pens, introduced in the second half of the 20th century and commonly used by modern and contemporary artists. These media of both drawing and writing have not yet been fully investigated, but the degradation processes they might undergo, such as fading, are well-known and rather apparent.

Twelve water-based felt-tip pens were investigated by the joint use of complementary analytical techniques, such as Thin Layer Chromatography, Nuclear Magnetic Resonance, Fourier transformed Infrared spectroscopy, X-Ray Fluorescence spectrometry and Pyrolysis-Gas Chromatography/Mass Spectrometry.

The obtained results provided crucial, preliminary data for the identification of dyes, solvents and additives present in the inks' formulations. Numerous synthetic food colouring agents and pigments were identified, such as Acid yellow 23, Acid Red 18, Acid Blue 9, Pigment Blue 15. In addition, glycols, fatty acids, 2-phenoxyethanol, colophony, benzotriazole derivatives and other solvents and additives were detected in the manufactured inks.

Furthermore, the effects of photo-degradation on one emblematic ink sample were studied, highlighting in particular visual and aesthetical changes due to discolouration.

This study demonstrates a methodology based upon the use of an integrated analytical approach for the characterisation of commercial ink-based artistic media and their viable degradation patterns, which aims to develop suitable conservation treatments to assess modern and contemporary drawings and writings.

Keywords: *Felt-tip pen; Organic dyes; Contemporary art; artificial ageing; FT-IR; Py-GC-MS; NMR*

1.Introduction

Over the last 50 years, artists have been experimenting with new materials, including those that were not specifically established for artistic purposes. Aesthetic effects, availability and low costs have often influenced artistic choice, at times over durability and stability over time. As a consequence, many contemporary materials, employed within artworks, have already undergone drastic deterioration and changes in appearance [1-3]. Such unexpected, rapid degradation raised some of the most complex and yet still unresolved questions regarding the conservation of these artworks. Knowledge of composition is the first and foremost step in order to understand the chemical behaviour over time. This concerns the development of the correct method of conservation, or at least the a procedure to slow the degradation processes down.

In this study we focus on felt-tip pens, introduced in the second half of the 20th century and used for both drawing and writing. The use of these media had become rather common amongst artists: for instance, Giuseppe Capogrossi (1900-1972), Jean Dubuffet (1901-1985) and Alighiero Boetti (1940-1994). Artworks produced from felt-tip pens are nowadays often found in a substantial amount of museum's collections all over the world.

A survey carried out by the authors within the collection of the "Gabinetto di Stampe e Disegni" (Prints & Drawings Cabinet) of the International Gallery of Modern Art Ca' Pesaro of Venice is illustrative of the presence of this particular technique in more than 30 drawings [4].
Despite the fact that felt-tip pens have been commonly used for a variety of different purposes, very few scientific works address this particular subject. Perhaps this is due to the fact that the inks' composition is often protected by trade secret and is very much dependant on the brand and year of production, thus consequently lacking in detailed chemical information or specific datasheets.
Some information can be found amongst forensic literature, as the authentication of documents is based upon both characterization and dating of the inks [5]. However, these studies are more often focused on other writing instruments, such as ballpoints, rollerballs and gel pens. For such investigations, different optical and chemical techniques can be employed, including Fourier transform infrared spectroscopy (FTIR) [6], Raman spectroscopy and surface-enhanced Raman scattering [7], laser desorption ionization- and quadruple-time of flight mass spectrometry [8], HPLC [9] and GC/MS [10]. Some felt-tip pens have already been analysed by Raman spectroscopy in order to identify the dyes [11]. Commercial inks are usually a mixture of organic dyes, solvents and additives [12] and thus chromatographic techniques are required in order to separate the different components, similar to that which was carried out on a number of permanent markers [13] and synthetic organic pigments in modern art [14-15].
The most common used felt-tip pens are based upon organic dyes and are known to be extremely sensitive to light (or photosensitive). According to Italian legalisation [16], such inks are situated between levels 1-3 on the Blue Wool scale for light fastness [17]. The principal degradation phenomena due to light exposition are in fact fading and discoloration.
Accelerated ageing by irradiation is a common practice in order to clarify the degradation mechanism of materials used in works of art [18,19] and can be useful to study general writing instruments as well [9, 20, 21]. Pure dyes have been investigated using this method [6, 18, 21], however dyes that are not mixed in the same manner as felt-tip pen inks. The reliability of this practice can only be validated on a case-by-case basis, due to the extreme conditions often required in order to extrapolate data on natural ageing from certain materials [22]. However, this is not the case when dealing with instable or fugitive materials, such as felt-tips pen inks, and so there is no need for the test to be assessed [23].
We report a detailed investigation on blue, black and red water-based felt-tip pens by means of different complementary techniques: Thin Layer Chromatography (TLC), Nuclear Magnetic Resonance (NMR), FTIR spectroscopy, X-ray fluorescence (XRF) spectrometry and Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS).
Four manufactured brands were selected, namely Stabilo (Germany), Giotto (Italy), Lyra (Italy) and , Pentel (Japan), as indicated by by the artistic collective Studio Fludd as the most accessible within in Italian art suppliers and the most commonly used by young artists [24].
Following with the identification of pigments, solvents and additives in the inks composition, one emblematic ink sample was then selected and exposed to artificial photo-degradation treatment, in order to gain more insights into its degradation mechanism.

2.Material and methods

2.1. Felt-tip pen ink samples

For this study, twelve water-based markers from four different manufacturers, commonly available amongst art suppliers, were selected and purchased in order to examine their inks. The commercial details are reported in Table 1.

<place table 1 here>

2.2. Sample preparation and analytical techniques

Thin Layer Chromatography (TLC)

Analytical TLC analyses were carried out on Machery–Nagel ALUGRAM® Xtra SIL G/UV_{254} pre-coated aluminum plates with 0.2 mm thick silica gel. The samples have been deposited on the plates from MeOH solutions. Two different

eluent mixtures were used: one acidic, nBuOH: H_2O:CH_3COOH 60:24:16 v/v (eluent A), the other basic, nBuOH:EtOH:NH3 5:2:3 v/v (eluent B). Each run was repeated several times in order to verify the reproducibility of the results.
Selected inks (samples GBk, GR, PB and PR) have been extracted from the pens' felts using MeOH and the solvent has been removed under vacuum, at 40 °C, and then freeze-dried (Lio 5P), in order to remove H_2O. For samples GBk and PR, the mixture has then been separated by preparative TLC (Analtech Uniplate SIL GF/UV254 pre-coated glass plates with 1.5 mm thick silica gel), on a few tens of mg scale, using eluent mixture B, and redissolving the coloured fractions in MeOH.

X-ray fluorescence spectrometry (XRF)
The elemental composition of the ink samples was analysed using energy dispersive X-ray fluorescence spectrometry, performed on the inks applied to disks of filter paper (i.e. no interference of elements). Measurements were performed on a Philips MiniPal X-ray fluorescence spectrometer with a rhodium cathode and operating at 20-40 keV. The identification of elements was obtained using Minipal software.

Fourier-transform Infrared spectrometry (FTIR)
Fourier-transform Infrared spectrometry was performed both in transmission mode (on ink samples applied as thin film on a KBr pellet) and ATR mode (on samples applied on watch glasses). Analyses were performed with a Thermo Nicolet Nexus 670 FTIR spectrophotometer combined with a Smart Orbit Single Reflection Diamond ATR accessory, from 4000 to 400 cm^{-1} for 64 scans with 4 cm^{-1} resolution. Spectra were elaborated with Omnic 6.0 and Origin 9.0 softwares.

Nuclear magnetic resonance (NMR)
1H-NMR spectra were recorded on CD_3OD solutions of the dried extracts or TLC fractions with a Varian Unity 400 MHz Spectrometer working at 25 °C.
Chemical shifts (δ) are reported in ppm using the solvent residual signal as internal reference (CD_3OD: δH = 3.31 ppm). Coupling constants (J) are given in Hz, and the resonance multiplicity is described as s (singlet), d (doublet), t (triplet) or m (multiplet).

Pyrolysis Gas Chromatography-Mass Spectrometry (Py-GC/MS)
In order to simultaneously detect both dyes and additives, all the samples were analysed using Thermally assisted Hydrolysis and Methylation Gas Chromatography-Mass Spectrometry (THM-GC-MS) in combination with pyrolysis. The inks were treated with a few drops of a 2.5% solution of tetra methyl ammonium hydroxide (TMAH) in methanol and transferred to a steel pyrolysis cup. The sample was pyrolysed at 550°C. Combining heat and reagent, pyrolysis, hydrolysis and methylation of the ink components took place. The total component mixture was separated by gas chromatography and the separated components are detected and identified with mass spectrometry.
A part of the inks were also analysed without TMAH to be able to show the presence of non-methylated and methylated components present within the inks.
The pyrolysis unit used was a Frontier Lab 3030D pyrolyser, mounted on a Thermo Scientific Focus GC / ISQ mass spectrometer combination. Separation took place on a SLB5 ms (Supelco) column with a length of 20 meters, an internal diameter of 0.18 mm and a film thickness of 0.18 µm. Helium was used as carrier with a constant flow of 0.9 ml/min. The temperature program set was 35 °C (1) – 60 °C /min – 110 °C – 14 °C/min – 240 °C – 5 °C/min – 315 °C (2). The column was directly coupled to the ion source of the mass spectrometer. The temperature of the interface was 240°C, the temperature of the ion source was 220 °C. Mass spectra were recorded from 29 until 600 amu with a speed of 7 scans per second. Xcalibur 2.1 software was used for collecting and processing mass spectral data.
All the pyrograms acquired were compared with a reference database of natural and synthetic pigments, both already available in literature and ad-hoc created by the authors.

2.3. Accelerating photo-degradation treatment and degradation evaluation

Accelerating photo-degratation treatment was performed on an emblematic ink sample, namely Giotto Black (GBk). The ink was applied a) on common white Fabriano© paper, b) as a thin film on a KBr pellet, c) on watch glasses. Furthermore, the three separated coloured fractions of this particular ink were applied on watch glasses and were additionally artificially aged.

Samples were exposed to an OSRAM Ultra-Vitalux® solar lamp (300 W, 230 V) at 50 cm of distance, in order to have upon the surface of the samples an illuminance of about 2000 lux, 40 times the value indicated as the maximum admitted in the Italian guidelines for museum exposition in the case of felt-tip pen drawings [16]. The wavelength of the light emitted was from 280 to 2000 nm (13.6 W in the range 315-400 nm, 3.0 W in the range 280-315).

The ink samples applied on paper were monitored after 0, 26, 48, 66, 88, 115, 139 and 160 hours by spectrocolorimetric measurements. A CM-2600d Konica Minolta spectrophotometer was used, operating in the wavelength range from 360 to 740 nm with 10 nm resolution. The colorimetric parameters L*a*b* (CIELab-space) and the reflectance spectra were recorded in SCI (specular component included) modality. The instrument has an 8-degree viewing angle geometry, with a Xenon lamp diffusion light and a high-resolution monolithic polychromator. Data were collected using Spectramagic software and elaborated with Origin 9.0 software. The total colour difference ΔE* was calculated according to equation $\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$ where ΔL*=L*(tx)-L*(t0); Δa*=a*(tx)-a*(0); Δb*=b*(tx)-b*(0) are the differences calculated for aged ink films (tx) and the original (t0) ink layer.

The ink samples applied on watch glasses were monitored after 48 and 168 hours by NMR and FTIR-ATR spectroscopy, whilst the samples applied on KBr pellets were monitored by FTIR in transmission mode.

3.Results and discussion

3.1. Formulation of felt-tip pen inks

Results on the composition of the analysed pen inks are shown in Table 2 and thereinafter separately discussed for dyes, pigments, solvents and additives.

<place table 2 here>

3.1.1 Dyes and Pigments

The first attempt to identify dyestuff present in the inks was performed by analytical TLC separation, which gave an overview of the complexity of the dyes' mixtures (Figure 1). The chromatographic elution with two different solvent mixtures, an acidic (eluent A) and a basic (eluent B), allowed for the comparison of the composition between the different commercial pen inks.

According to their retention factor, the same dyes have been found in different inks. In particular, samples SR, GR, LR, SBk, GBk and LBk contain the same red dye; moreover, SR, LR, GBk and LBk also obtain the same yellow dye. Samples GB, LB, PB, SBk, GBk, LBk and PBk contain the same blue dye (overlapped with an orange spot in PBk). Samples SB, PB and LBk contain the same pink dye, while GB, LB and PBk a purple dye.

Moreover, SB, SBk and PBk runs showed the presence of a coloured fraction which did not elute from the deposition spot (retention factor = 0). This suggests that the ink preparation of these pens contains some organic pigments in ultrafine dispersion. These pigments could tentatively be assumed to be Pigment Blue 15 for SB and Pigment Black 7 for SBk and PBk, which are known to be used in felt-tip pens' formulations [12].

Considering these results, two representative samples (GBk and PR) have been selected, as their composition would have allowed for the identification of most of the coloured fractions present in the whole set of samples, in addition to their dyes having been separated on a bigger scale by preparative TLC.

<place figure 1 here>

Figures 2 and 3 depict FTIR spectra of the single fractions and of some whole inks. The main IR absorptions are recognizable in all the spectra. However, their identification is not trivial in the spectra obtained from the whole inks, due to the overlapping of different bands (especially in the regions 1200-1000 cm^{-1} and 800-600 cm^{-1}).
On the other hand, FTIR analyses, of the three GBk coloured fractions, allowed a straightforward comparison with Thermo Scientific and SDBS reference spectra [25]. Thus, the red, yellow and blue dyes have been identified, respectively, as Acid Red 18 (1,3-Naphthalenedisulfonic acid, 7-hydroxy-8-[(4-sulfo-1-naphthalenyl) azo]-, trisodium salt also known as Ponceau 4R, Cochineal Red A), Acid Yellow 23 (1H-Pyrazole-3-carboxylic acid, 4,5-dihydro-5-oxo-1-(4-sulfophenyl)- 4-[(4-sulfophenyl)azo], trisodium salt also known as Tartrazine) and Acid Blue 9 (Benzenemethanaminium, N-ethyl-N-[4-[[4-[ethyl[(3- sulfophenyl)methyl]amino] phenyl](2-sulfophenyl)methylene]-2,5-cyclohexadien-1-ylidene]- 3-sulfo-, inner salt, diammonium salt also known as Erioglaucine).

<place figure 2 here>

<place figure 3 here>

1H-NMR analyses of the separated fractions confirmed the identification of the yellow and red dyes contained in GBk, and their spectra were fully assigned (Figure 4). On the contrary, it was not possible to unambiguously assign all the peaks given by the blue fraction, most likely due to the presence of other components eluting together with the blue dye, which gave partially overlapping NMR signals. Nevertheless, we compared this spectrum with the one of a compound differing from Acid Blue 9 only for two substituents, previously reported [26]. Owing to this comparison, it was possible to corroborate FTIR results, further supporting the identification of the blue fraction with Acid Blue 9. Additionally, the integrals ratio in the 1H-NMR spectrum of the whole ink permitted the estimate of the relative molar amounts of the three dyes in the mixture, which was found to be approximately 4:2:1, referred to the red:blue:yellow dyes (see supplementary data).

<place figure 4 here>

In the case of the pink fraction from sample PR (Figure 5), the FTIR spectrum demonstrated to be quite similar to the reference one of Acid Red 87 (disodium;2-(2,4,5,7-tetrabromo-3-oxido-6-oxoxanthen-9-yl) benzoate also known as Eosine Y). However, the presence of several different peaks, could be ascribed to Eosine tautomerism between a neutral, an anionic and a cationic species as reported in [27, 28]. In this case, the determination of the elemental composition through XRF analysis was crucial (Table 3), since it showed, for sample PR, the presence of bromine, confirming the identification of the pink fraction with Acid Red 87.

<place table 3 here>

<place figure 5 here>

Table 4 reports the main FT-IR absorption bands related to the identified dyes.

<place table 4 here>

The two azo dyes were identified with PY-GC/MS as well. In particular, the presence of AY 23 could be determined by comparison with the references. The main pyrolysis product is 4-methyl-benzenesulfonic acid, methyl ester (peak 7 displayed in Figure 6a), with molecular ion at m/z=186 and base peak a m/z=91. The azo red AR 18 was assigned thanks to the presence of naphthalene-based compounds (m/z= 89, 115, 128 and m/z=142, 172 and 157 - peaks 6, 8, 10 in Figure 6a). Py–GC/MS analysis not only confirmed the data previously obtained, but also provided useful data for the recognition of other dyes, by the identification of characteristic pyrolysis products.

Pyrogram of sample SB (Figure 6c) suggested the presence of a phthalocyanine. In fact, 1,2-benzenedicarbonitrile, reported as one of the principal pyrolysis products of phthalocyanine pigments [13], was found, and the analysis yielded methyl-isoindole which is another marker of phthalocyanines.

<place figure 6 here>

As a result of detection of copper by XRF (Table 3), the specific phthalocyanine pigment was subsequently identified to be Pigment Blue 15 (Figure 7a) or one of its phase-stabilized forms (P.B 15:1, P.B. 15:2, P.B. 15:3, 15:4) [29]. These findings are in perfect agreement with the hypothesis completed after the chromatographic run, as previously explained. Furthermore, in the same sample, the presence of quinoxaline carboxamide might derive from the fluorescent pink dye found in the TLC run, possibly ascribable to previously reported quinoxaline-based dyes [30-32]. In addition, in the pyrogram of the Pentel black-coloured felt-tip pen (Figure 6b), diphenylamine suggested the presence of a different kind of dye, such as aniline black (Pigment Black 1, Figure 7b).

<place figure 7 here>

3.1.2 Solvent and additives

Together with the strong absorption bands due to presence of dyes, all the FTIR spectra show the vibrational modes of other compounds.

The spectra of all the Giotto and Lyra samples show some characteristic peaks due to the presence of diethylene glycol: the strong absorption at 1125 cm^{-1} and at 1070 cm^{-1} due to the asymmetric and symmetric stretching of C-O-C, the -OH in-plane bending coupled with the C-H wagging vibration at 1458 cm^{-1} and 1350 cm^{-1} and the C-O stretching vibration at 924 cm^{-1} and 900 cm^{-1} diagnostic for primary alcohols.

In the Stabilo samples bands at 1350 cm^{-1}, 1122 cm^{-1} (strong) and at 945 cm^{-1}, 887 cm^{-1}, 830 cm^{-1} indicate the presence of polyethylene glycol (see Figure 3). 1H-NMR spectroscopy on CD_3OD solutions of the whole inks showed the typical peaks of ethylene glycolic derivatives in addition. In particular, the triplets at 3.56 and 3.68 ppm indicated the presence of diethylene glycol in samples GBk, GR and PB, while the singlet at 3.60 ppm in the spectrum of PB is ascribable to polyethylene glycol (see supplementary data).

Py-GC/MS analyses confirmed the obtained results and enabled the identification of other compounds, present in a small amount in the ink formulations. Diethylene glycol was identified both in the methylated form and the non-methylated one (peaks 2 and 3, Figure 6 a). Polyethylene glycol is recognisable from the presence of a series of peaks with the same mass spectra due to the fragmentations of the polymer methylated and the subsequent losses of-CH_2OCH_3 (Figure 6c).

Other glycols, namely ethylene glycol and glycerol, have been identified in the Pentel and Stabilo red and black inks, respectively. Pyrograms of Lyra samples showed at Rt 13.32 min the methylated form of the dehydroabietic acid (Figure 6a), one of the most important markers of diterpenic resins [33]. This compound might indicate the presence in the ink of colophony, one of the additives also present in permanent markers [34].

Pyrograms of Lyra and Pentel samples showed two peaks, at Rt 4.81 and 4.90 min, due to 2-phenoxyethanol and its methylated form (Figure 6a and b), a preservative and antimicrobial also used for dating ballpoint pen inks [5].

Analyses of Pentel samples showed at 4.70 min and 6.16 min two different 1H-benzotriazole methylated forms (peaks 4 and 5, Figure 6b). This compound may have originated from the fragmentation of TINUVIN® 328 or similar derivatives, used as ultraviolet light absorbers for a variety of substrates.

Finally, in all the pyrograms three peaks at 7.57 min, 10.50 min and 11.86 min, due to the methylated form of azelaic acid, palmitic acid and stearic acid indicate the presence of free fatty acids, probably used as lubricants having been previously discovered amongst ballpoint pen inks [35].

3.2 Accelerating photo-degradation treatment

After 160 hours of light exposure, GBk ink applied on paper showed a significant change in colour (Figure 8a), which is clearly described to the changes of the colorimetric parameters (Figure 8b). The ink layer demonstrated a total of colour differences (ΔE) greater than 30, mainly due to the contribution of Lightness, L*. The increase of ΔL indicates

that the main degradation effect was fading. Alterations of a* and b* are evident as well. In particular, the increase of b* indicated a change to yellow while the decrease of a* is related to a shift to a green colour.

<place figure 8 here>

Variations are recognisable also in the reflectance spectra (Figure 8c). The original GBk ink film is characterized by a dominant reflectance around 740 nm together with low reflectance peaks at 440 nm and 580 nm, due to the red, yellow and blue, respectively. Following the ageing procedure, the spectra showed an increased reflectance together with the gradual disappearance of the peak at 440 nm (blue). Formation of a new band at 510 nm (green) was measured in addition.
The ΔL*, Δa* and Δb* colour differences, monitored during photo-degradation treatment, reflect the changes in the chemical structure of ink, as shown in Figure 9. The main changes in the FTIR spectra are the disappearance of three bands (1126 cm^{-1}, 1070 cm^{-1} and 900 cm^{-1}) due to the degradation of diethylene glycol. As a consequence, two peaks at 1145 cm^{-1} and 1120 cm^{-1} were detected, after 48 hours of light-exposure, due to the red and the yellow dyes, respectively: these signals were previously hidden by the adsorption of glycol (band at 1126 cm^{-1}). The absence of new bands indicates the decomposition of DEG in volatile products during light exposure. After 168 hours of light-exposure, the band at 1408 cm^{-1} was not detectable anymore, whilst the band at 1582 cm^{-1} (related to vibrations of the aromatic ring) was noticeably decreasing in intensity. These peaks were previously attributed to the blue dye A.B. 9: this might indicate a change in the structure of the compound due to the photo-oxidative treatment.
FTIR analysis of the separated fractions of GBk confirmed this interpretation: the peak at 1072 cm^{-1}, previously hidden by the DEG bands, and the one at 1408 cm^{-1} are due to the C-H bending vibration and their decrease indicate a partial loss of the ethyl group, as already reported for Acid Blue 9 [36] and other dyes of similar structure [18].
<place figure 9 here>

This hypothesis was further strengthened by 1H-NMR spectroscopy, since the signals due to the ethyl groups (400 MHz, CD_3OD, δ = 3.77 (q), 1.31 (t) ppm) gradually decreased in intensity with respect to the rest of the molecule, as the ageing time increased. Moreover, many new peaks appeared in the aromatic region of the spectrum, clearly indicating the occurrence of decomposition (Figure 10).

<place figure 10 here>

On the other hand, as far as the fractions containing Acid Red 18 and Acid Yellow 23 are concerned, both FTIR and NMR analyses remained unchanged. These results indicated that no registered degradation process occurred for these two dyes in the conditions generated.

4.Conclusions and Future perspectives

This research provides crucial preliminary data for both the identification of commercial ink-based artistic media and their potential degradation patterns, which aims to develop suitable conservation treatments in order to assess modern and contemporary drawings and writings.
Throughout this study, the focus was placed upon the composition of several of the most commonly utilised modern felt-tip pen inks. However those that are predominantly covered by trade secret, thus hindering a complete understanding of the degradation processes taking place. The application of different complementary techniques was crucial to achieve this goal. In fact, TLC, Py-GC/MS, XRF, FTIR and NMR spectroscopies permitted the identification of a substantial amount of the colour agents, solvents and additives within 12 markers from Pentel (Japan), Stabilo (Germany), Giotto (Italy) and Lyra (Italy) brands.
Preliminarily, TLC enabled the identification of the number and colours of the commercial dyes used. Py-GC/MS was overall the most enlightening technique, as it enabled the identification of both solvents and dyes, as well as the additives present in a smaller amount. On account of the high level of fragmentation achieved with such techniques

and subsequentely the necessity of a suitable database, FT-IR and NMR were effective at confirming such results, following the prior separation of the samples. Finally, despite the fact that the elemental composition resulted similarly to the majority of the samples, XRF analysis was crucial for the identification of specific metal stabilized forms.

Regarding the dyes, several synthetic food colouring agents were identified, namely Tartrazine (Acid yellow 23), Ponceau 4R (Acid Red 18) and Erioglaucine (Acid Blue 9), together with Acid Red 87. Moreover, some pigments were also discovered, such as Pigment Blue 15.

Solvents and additives, such as glycols and fatty acids, were found indiscriminately amongst all the samples. On the contrary, 2-phenoxyethanol was identified only in Lyra and Pentel samples, while colophony was found to be characteristic of Lyra samples, therefore these two compounds are diagnostic for these two brands. The presence of an ultraviolet light absorber, namely a benzotriazole derivative, was recognized only in the Pentel samples and in the blue ink of the Giotto brand.

The photo-ageing treatment of the emblematic Giotto black ink demonstrated that the different dyes present may be affected to different extents. Under the appointed ageing conditions, only the blue fraction of the ink was undergoing some decomposition, whilst the red and yellow ones appeared to remain stable. Furthermore, it should be emphasized that visual and aesthetical changes are noticeable in an extremely short time, since ΔE values larger than 5 were recorded after less than 24 hours of solar lamp exposure.

The finding of the study reveals the importance for contemporary artists to choose high quality media for drawing and writing, for example, inks containing preservatives and UV-absorbers. Moreover, in order to increase the lifetime of felt-tip pen-based artworks, one could envisage the possibility to develop conservation treatments with light stabilizers, when they are not originally present, something that is currently under study within our research institutes.

Acknowledgments

The authors express their thanks to Dr. Matteo Piccolo of the International Gallery of Modern Art in Ca' Pesaro (Venice) for the interest demonstrated for the study and the interaction between art and conservation science.

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Figure1

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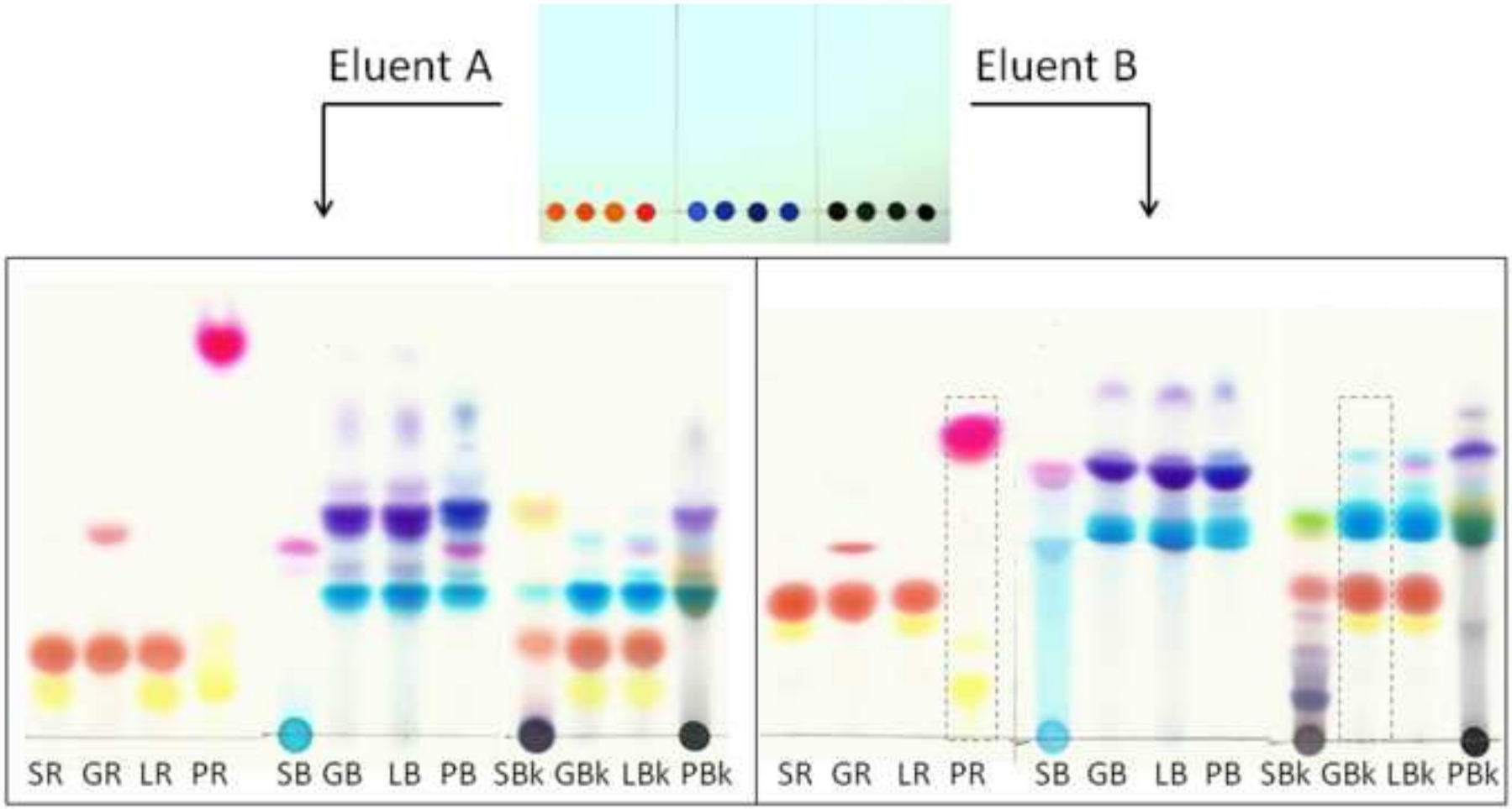

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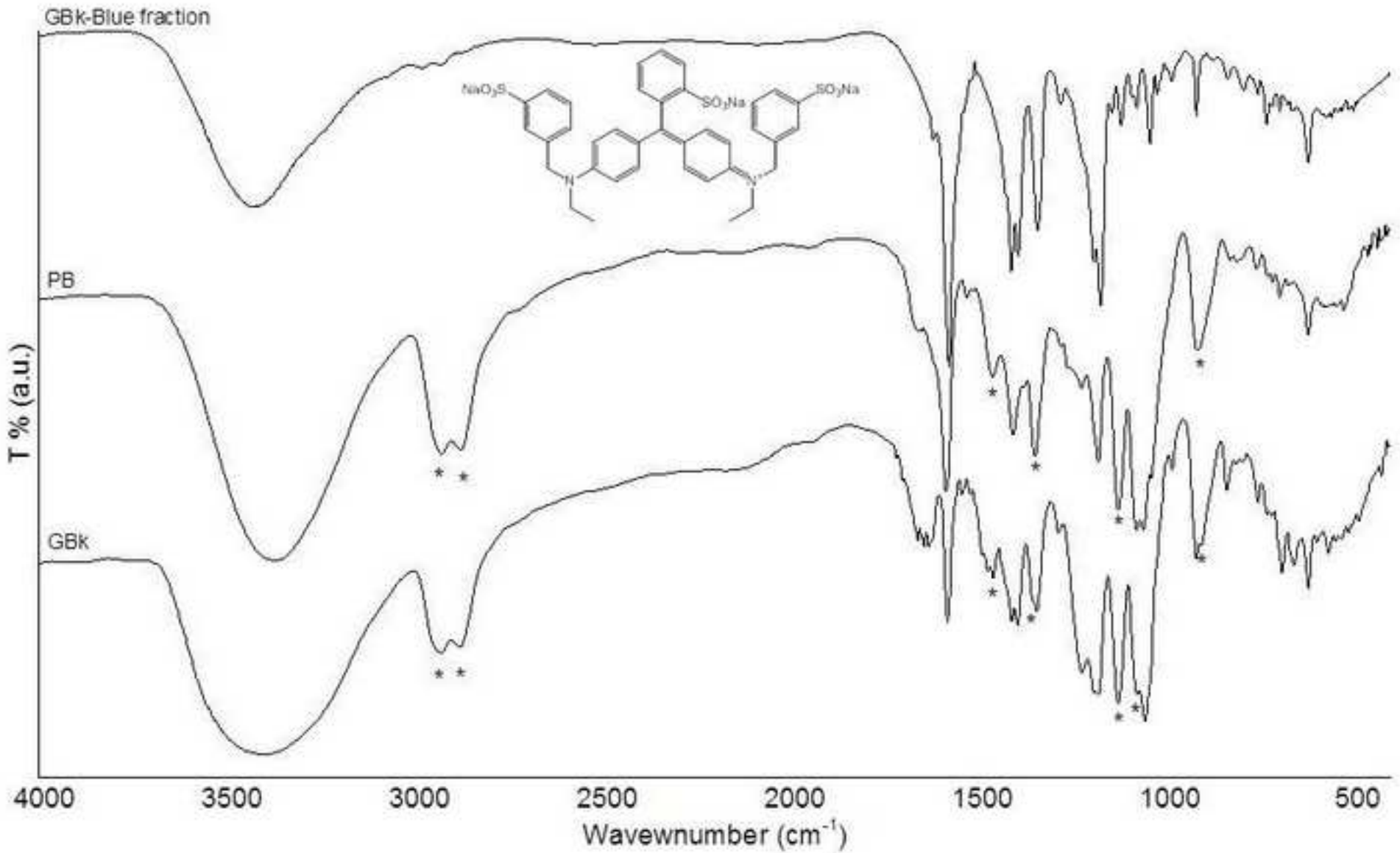

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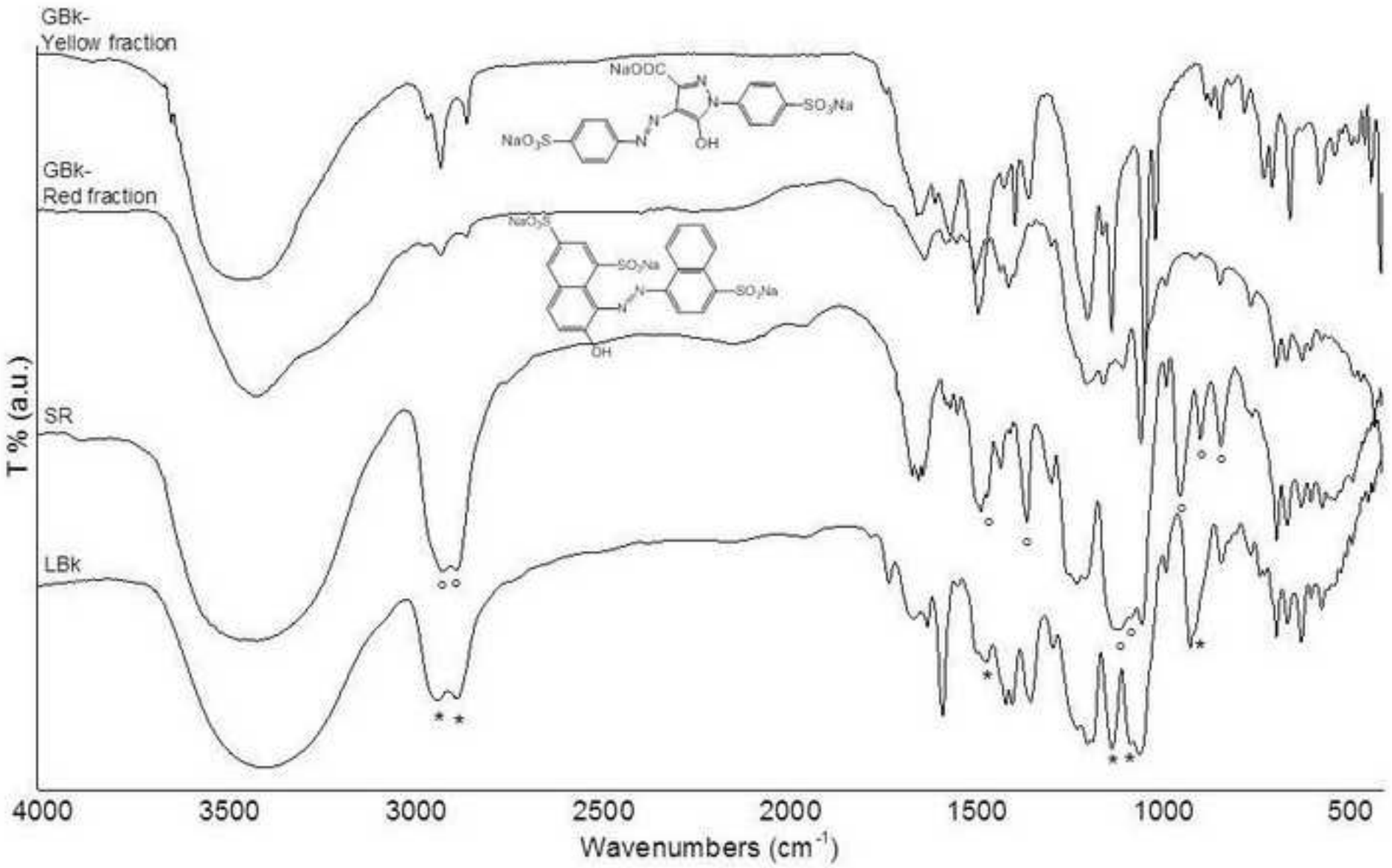

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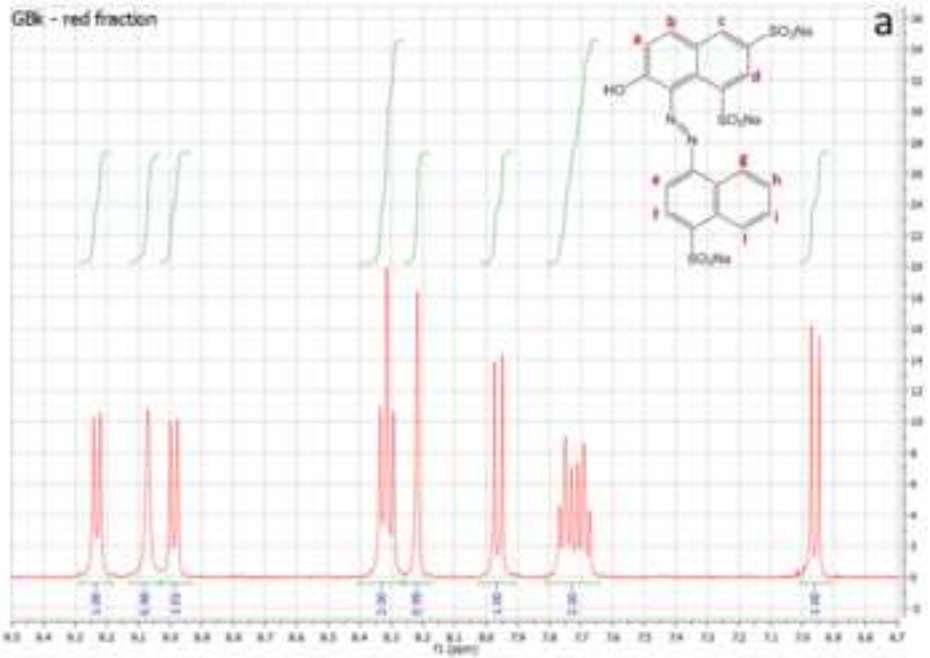
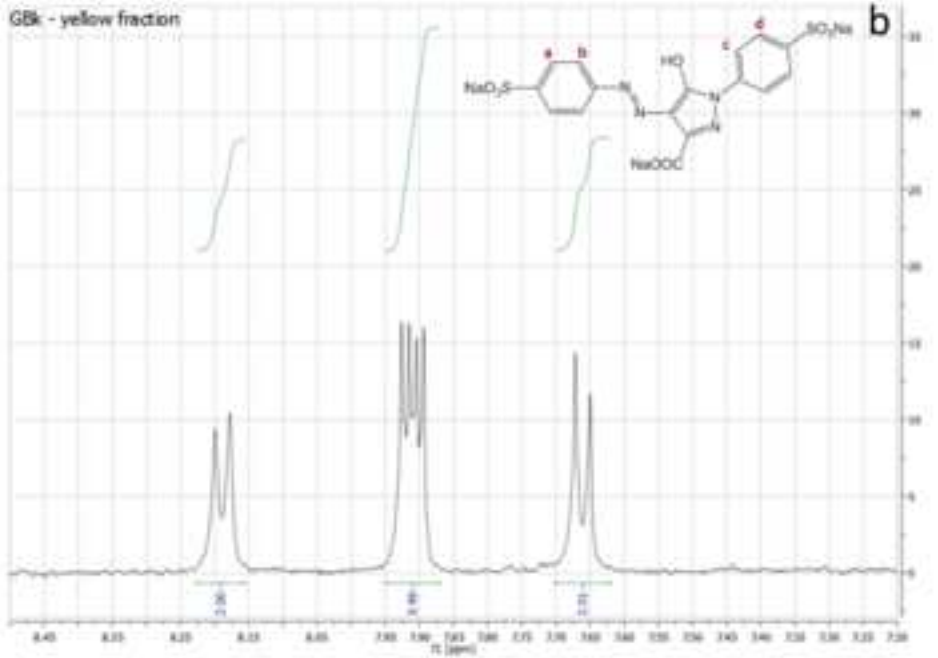


1H NMR (400 MHz, CD_3OD): δ = 8.24 (d, J = 8.2 Hz, 1 H, Hc), 8.08 (s, 1 H, Hd), 8.59 (d, J = 8.2, 1 H, Hf), 8.52 (t, J = 8.4 Hz, 2 H, Hg,h), 8.22 (s, 1 H, Hc), 7.97 (d, J = 9.5 Hz, 1 H, Hb), 7.85-7.80 (m, 2 H, Hg,i), 6.96 (d, J = 9.5 Hz, 1 H, Ha) ppm.



1H NMR (400 MHz, CD_3OD): δ = 8.20 (d, J = 8.8 Hz, 2 H, Hc), 7.96 - 7.88 (m, 4 H, Ha,d), 7.67(d, J = 8.8 Hz, 2 H, Hb) ppm.

Figure 5

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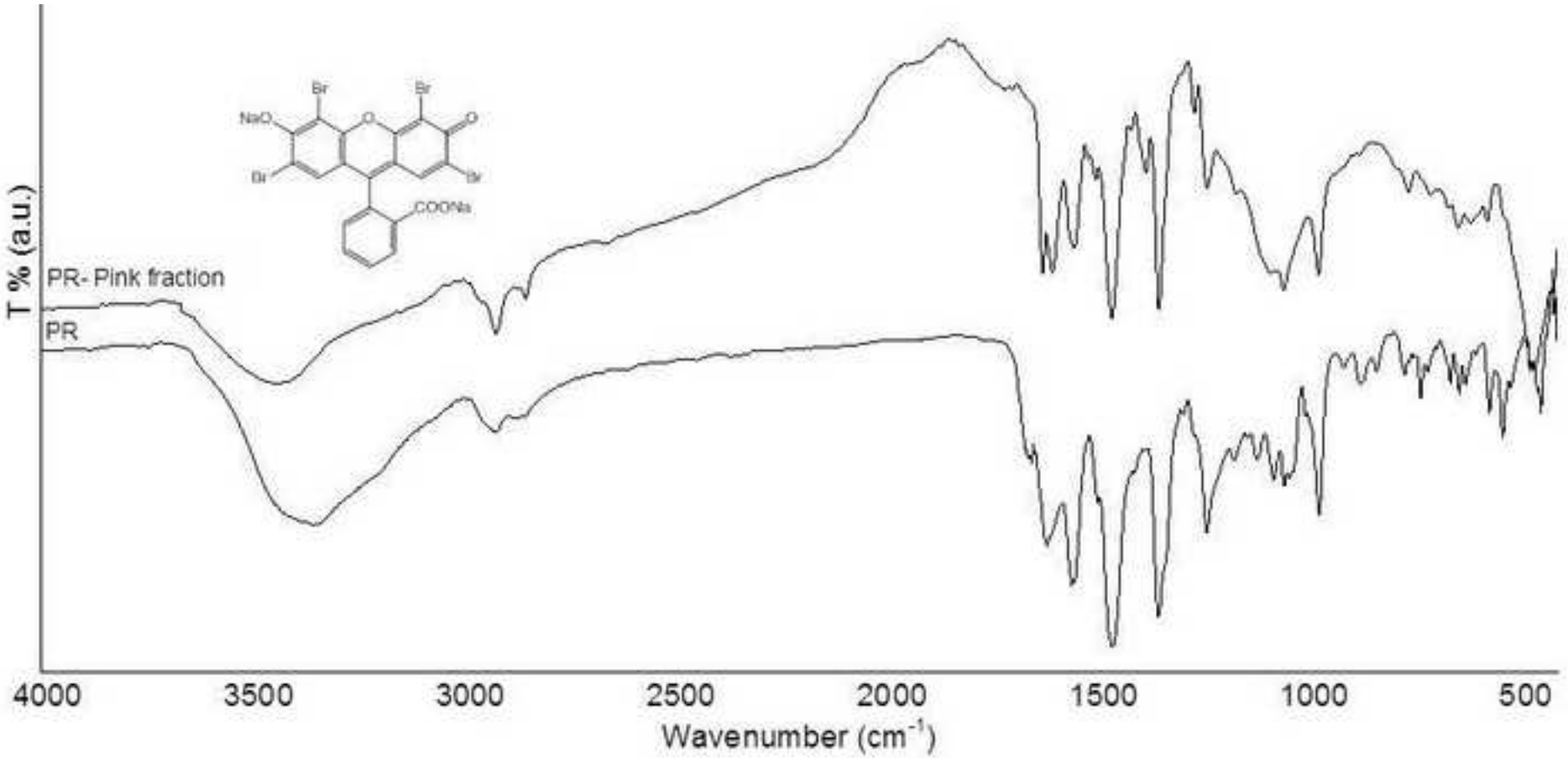

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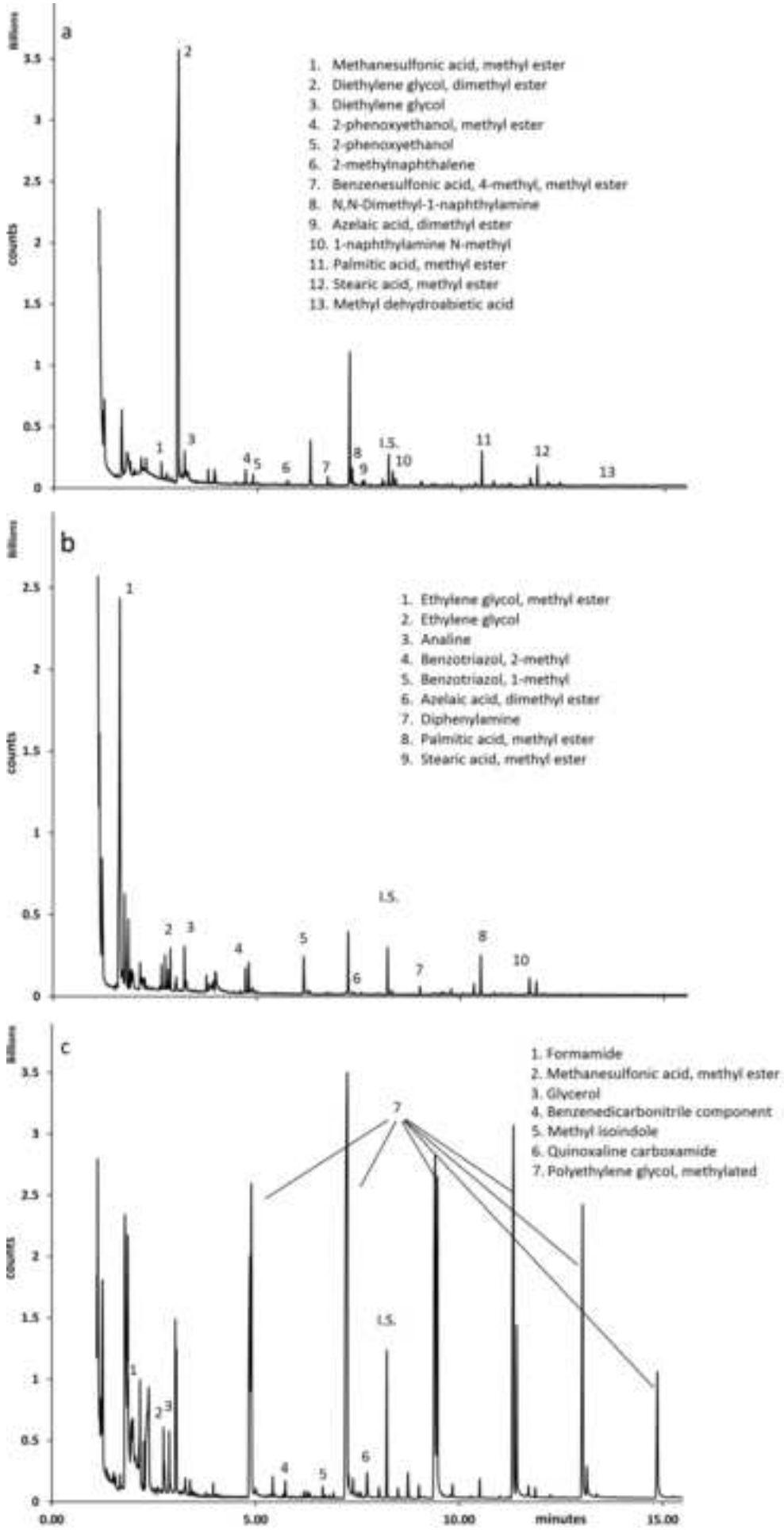

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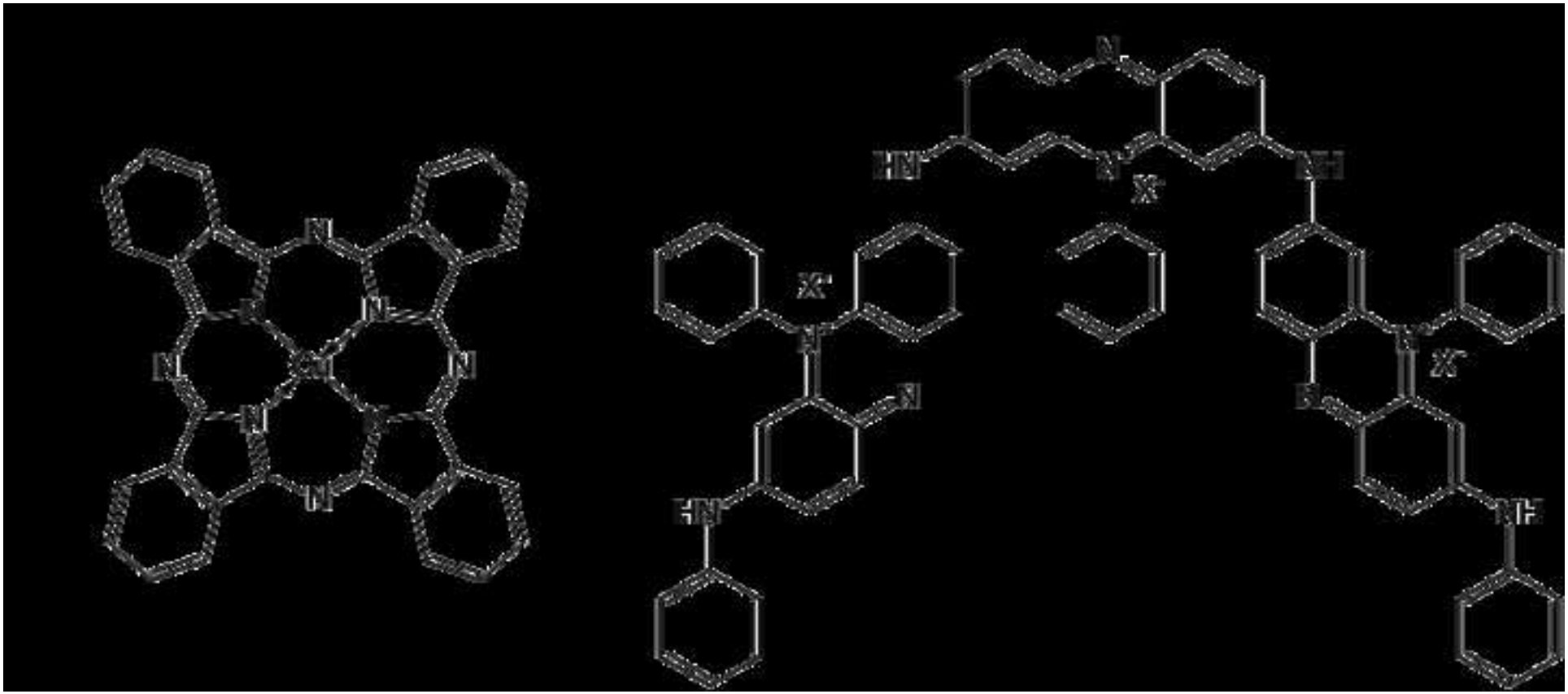

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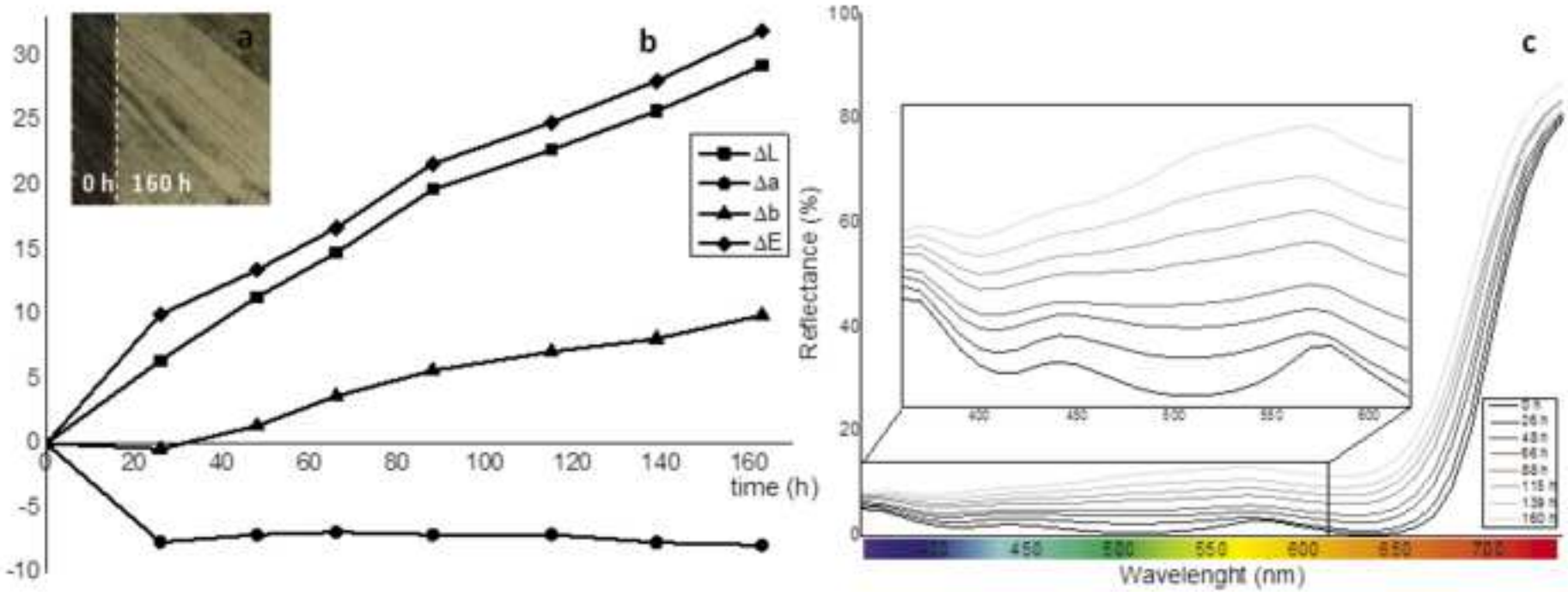

Figure 9

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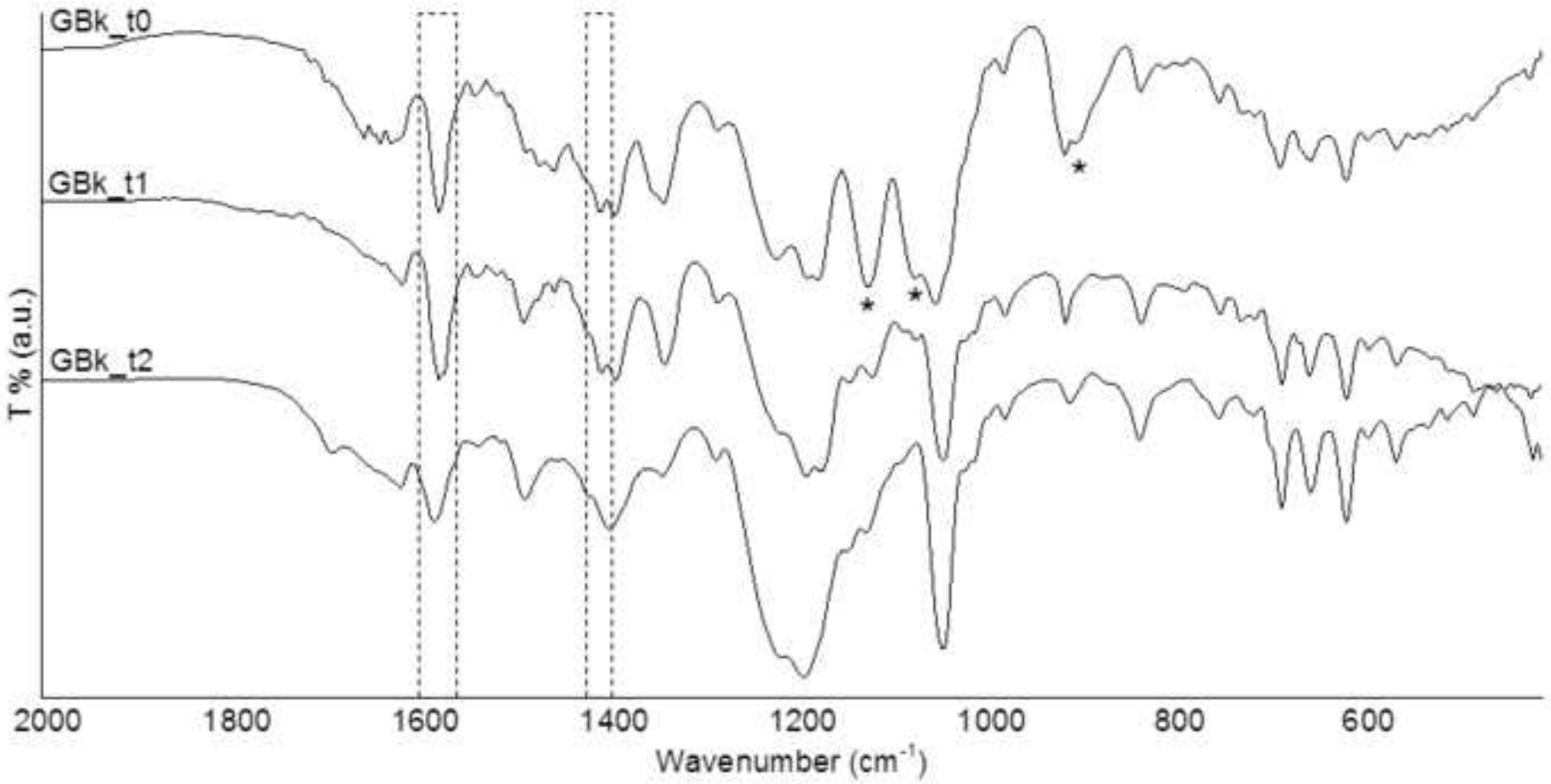

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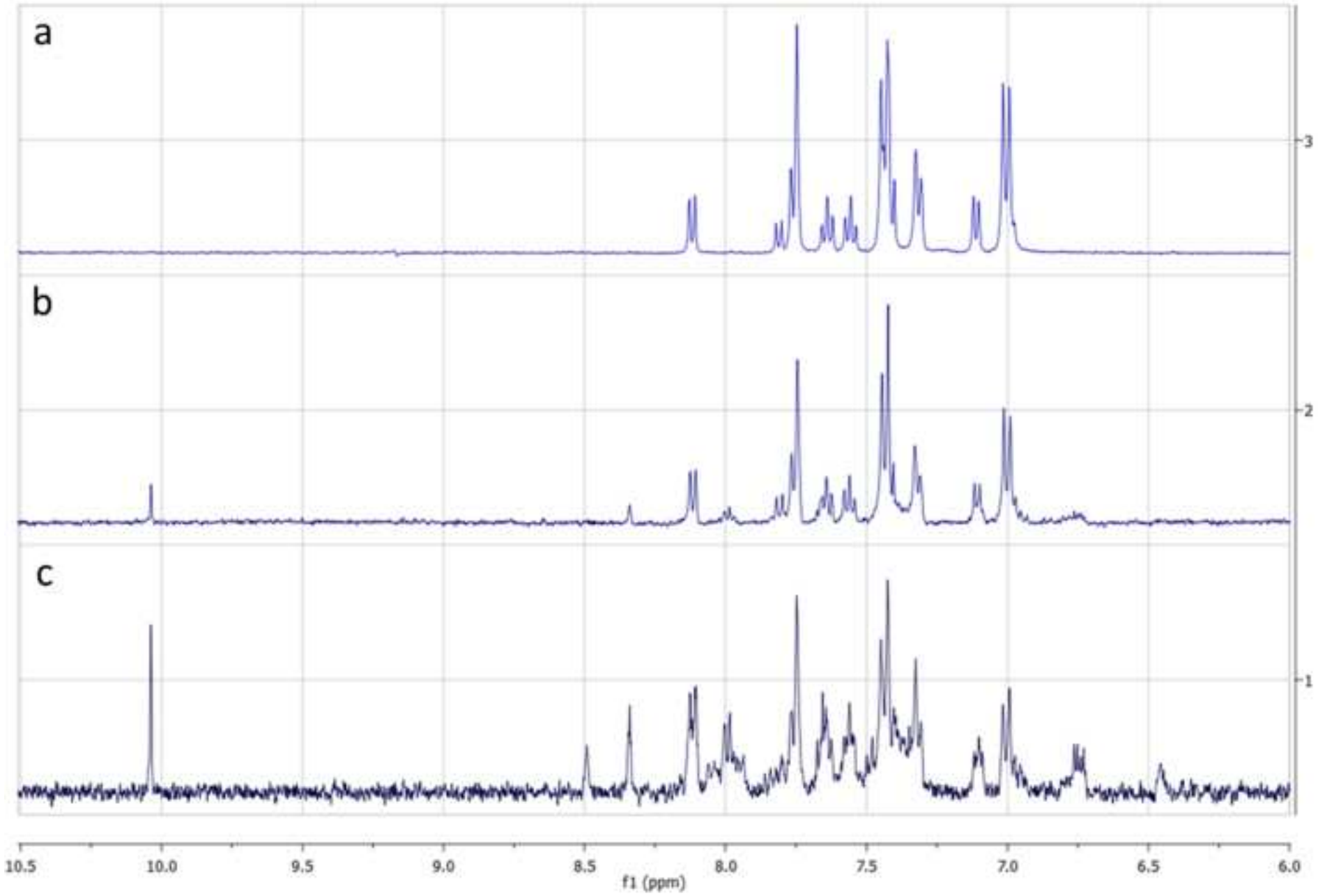

Captions for figures

Figure 1: Comparison of TLC separation using acid eluent (A) and basic eluent (B). In the boxes: inks selected for preparative TLC.

Figure 2: Infrared spectra of blue fraction from GBk sample, PB and GBk inks highlighting the presence of Acid Blue 9 and of diethylene glycol (* bands).

Figure 2: Infrared spectra of yellow and red fraction from GBk sample, SR and LBk inks highlighting the presence of Acid Yellow 23, Acid Red 18, diethylene glycol (* bands) and polyethylene glycol (° bands).

Figure 4: 1H-NMR spectra of red (a) and yellow (b) fractions of sample GBk.

Figure 5: Infrared spectra of pink fraction from sample PR and PR ink.

Figure 6: Pyrograms of samples a) LR, b) PBk and c) SB. Peak numbers correspond to the main identified compounds (IS=internal standard).

Figure 7: Structures of the colorants Pigment Blue 15 (a) and Pigment Black 1 (b).

Figure 3: Macroscopic (a), colorimetric parameters (b), reflectance spectra (c) changes after accelerated photo-degradation treatment.

Figure 4: Infrared spectra (transmission mode) of sample GBk after 0 (t0), 48 (t1), 168 (t2) hours of lamp exposure (* bands from diethylene glycol). In the boxes: peaks enlightening changes in AB 9 structure.

Figure 10: 1H-NMR spectra of the blue fraction of sample GBk before (a) and after 48 hours (b) and 168 hours (c) of artificial light ageing.

Supplementary Figures

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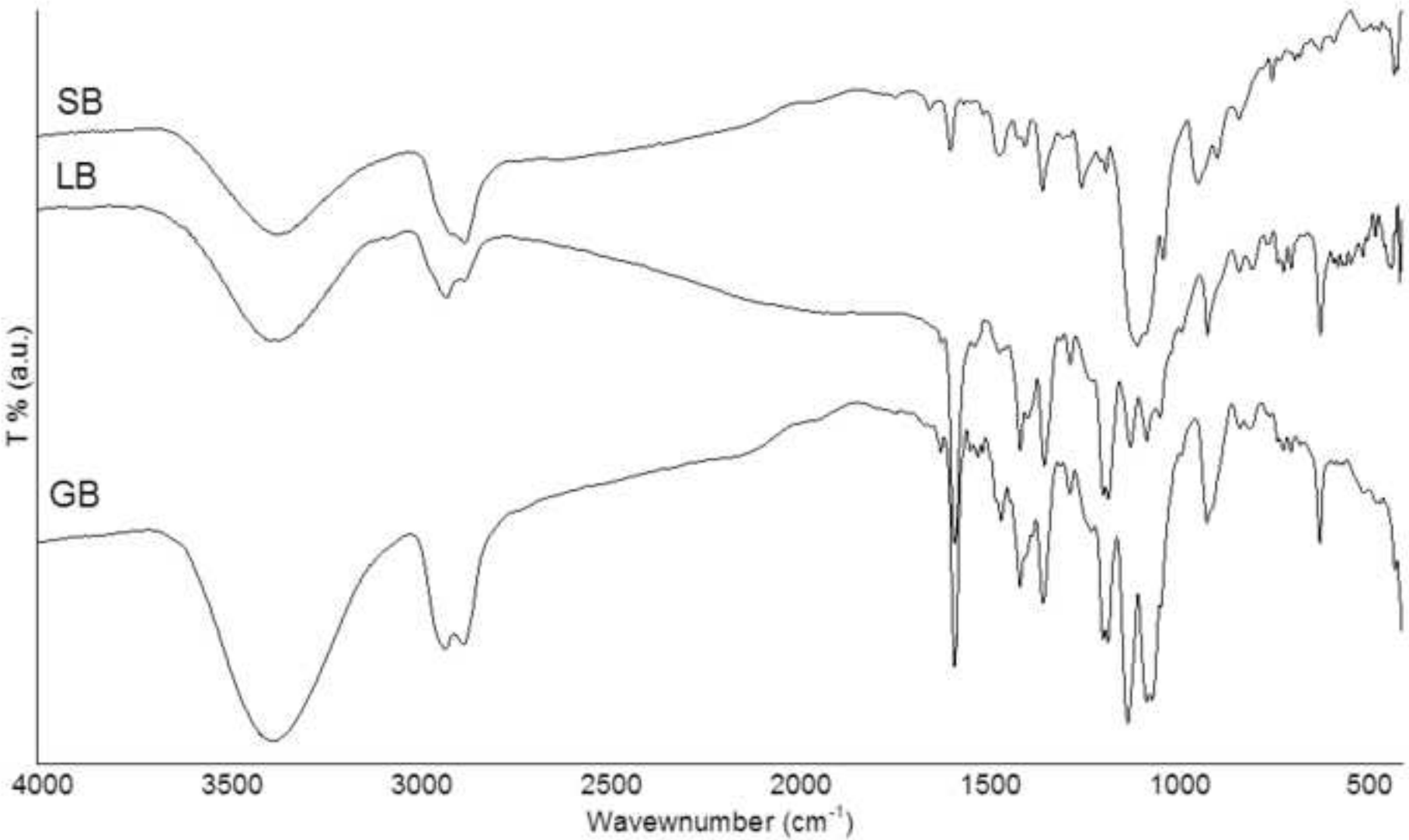

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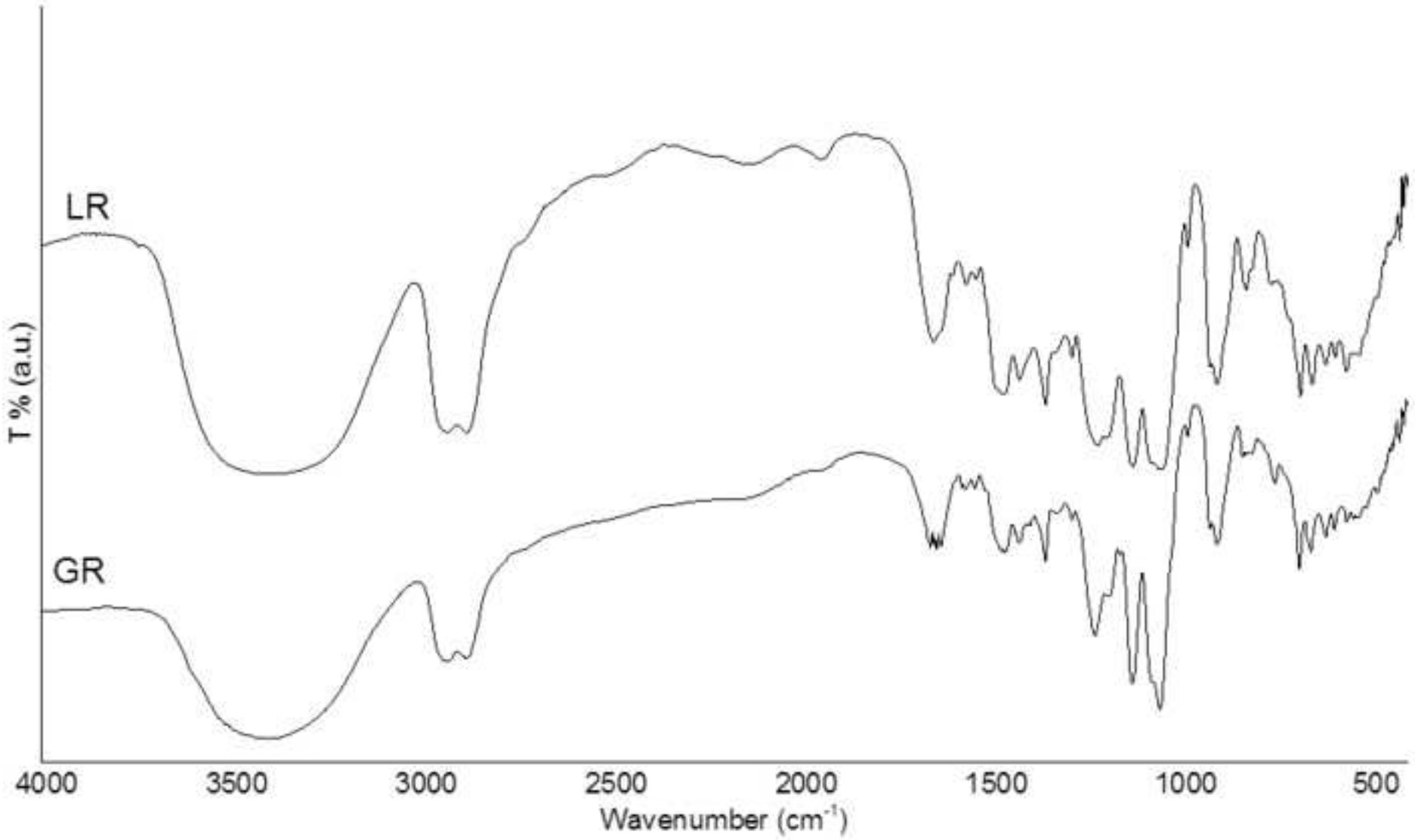

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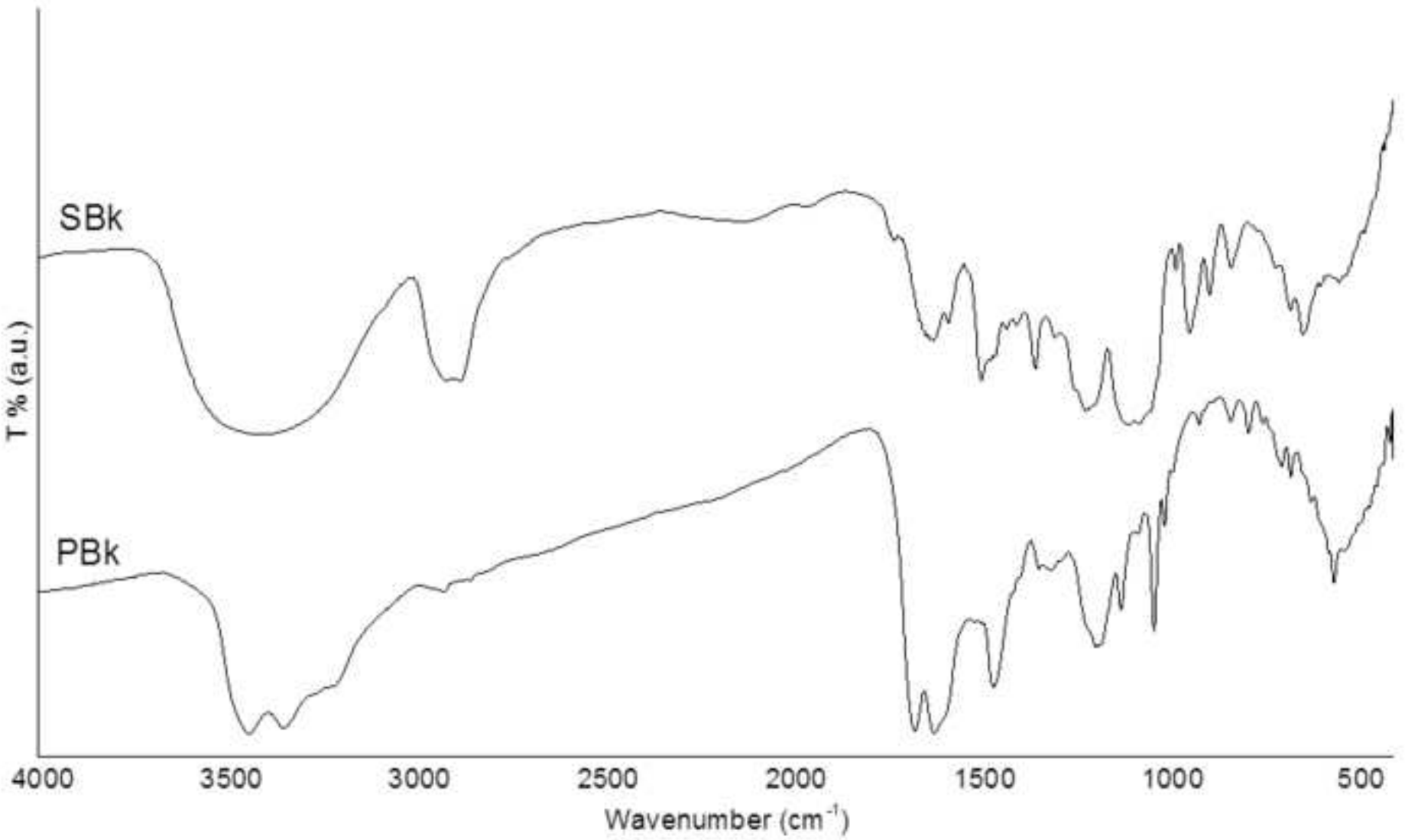

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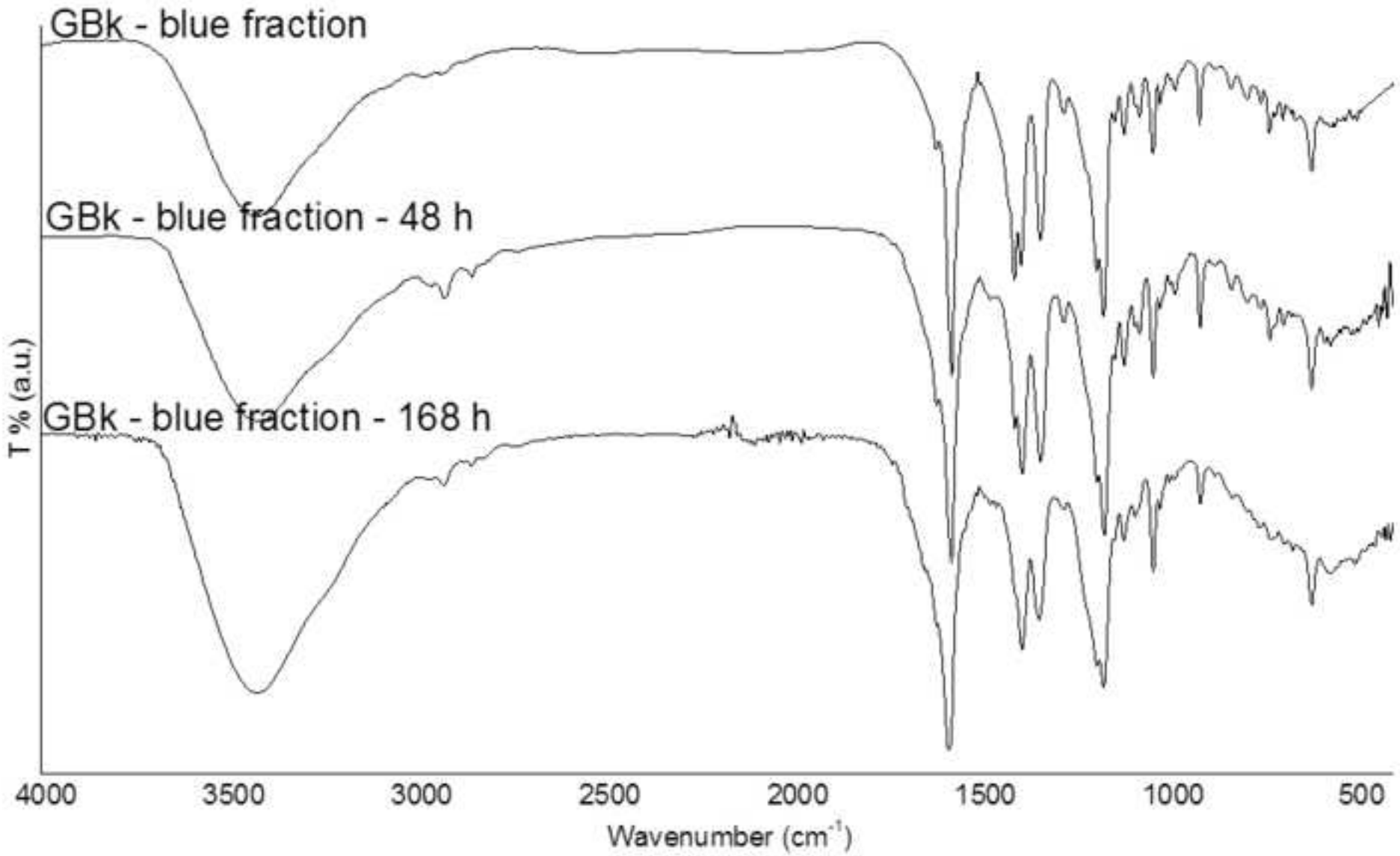

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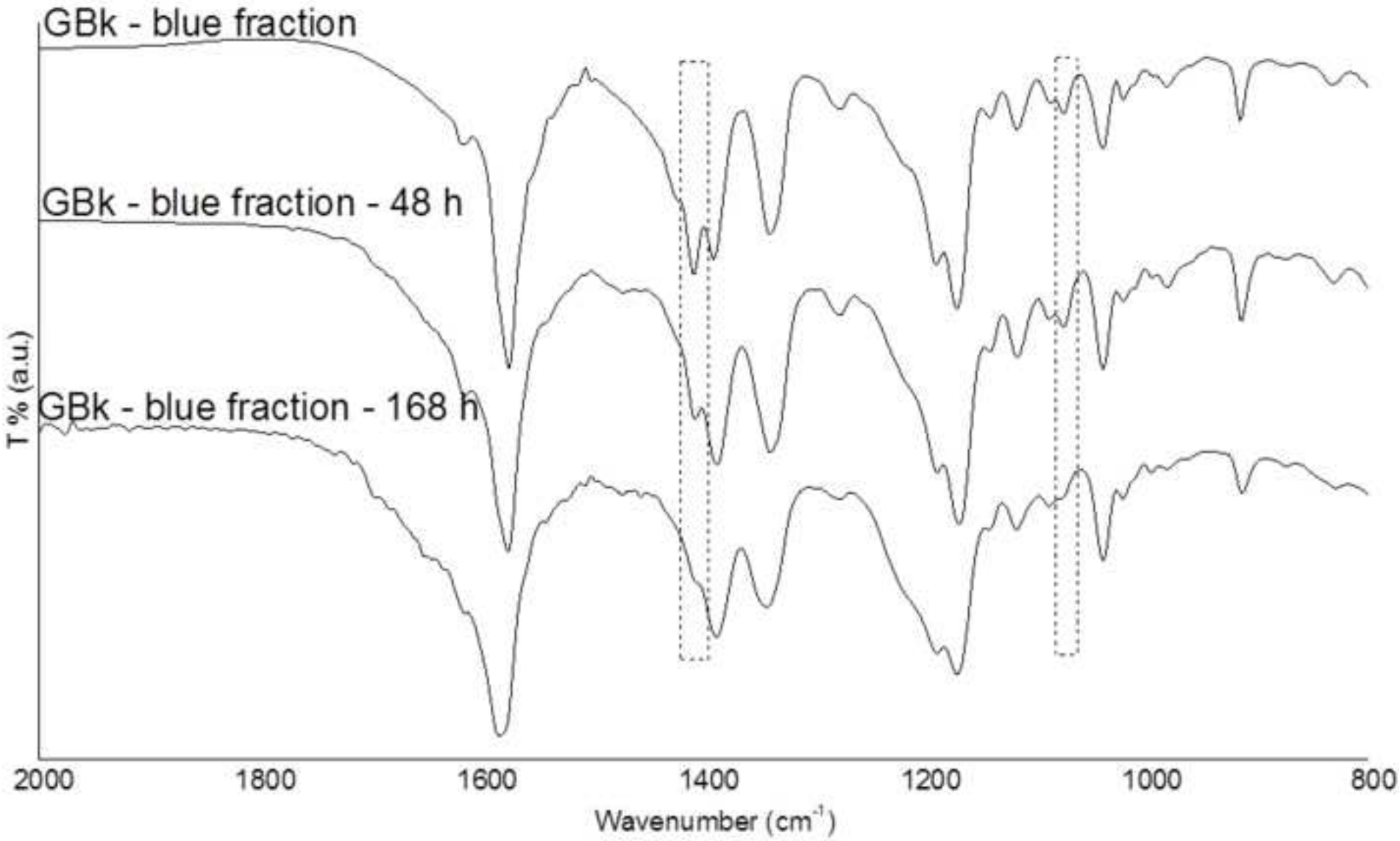

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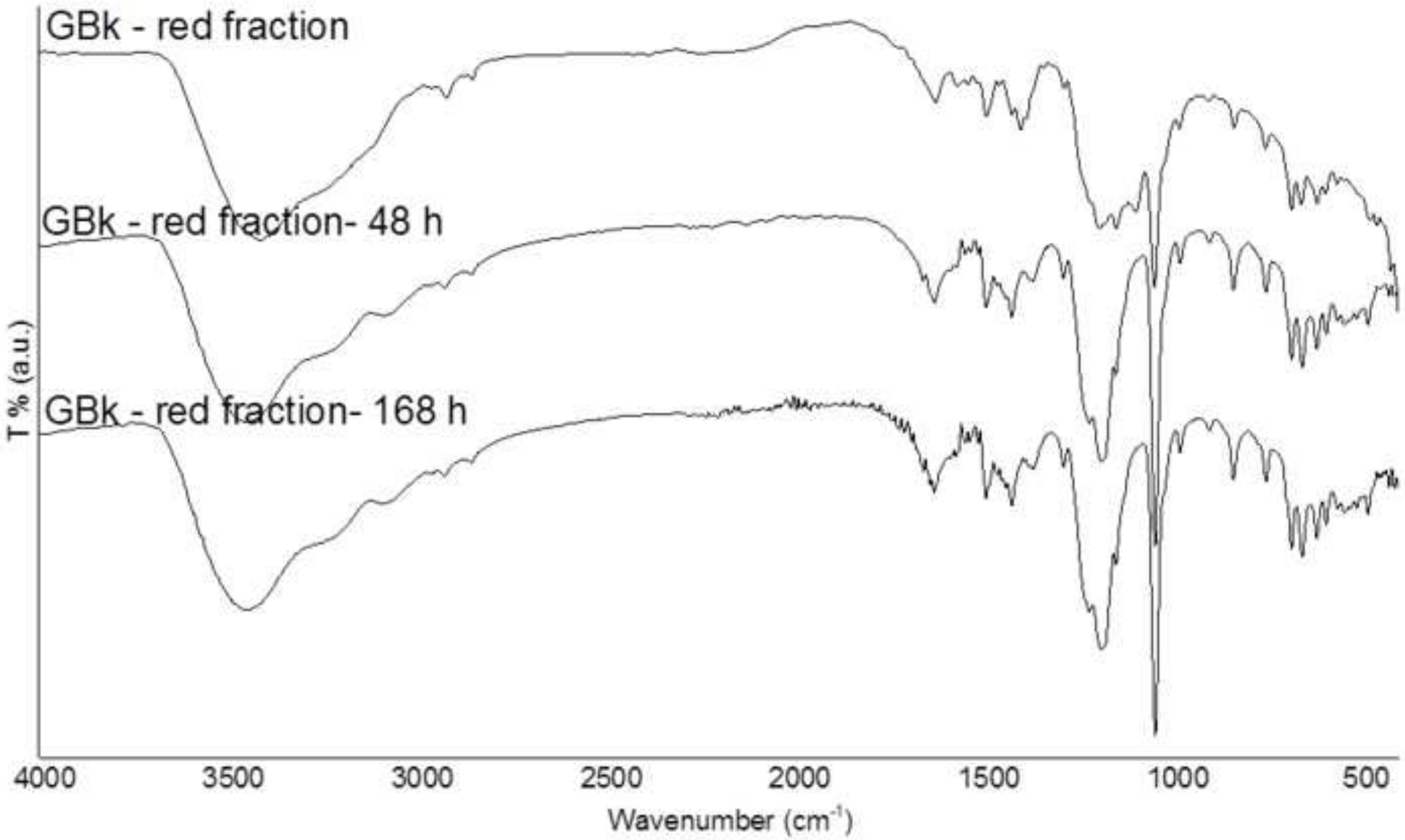

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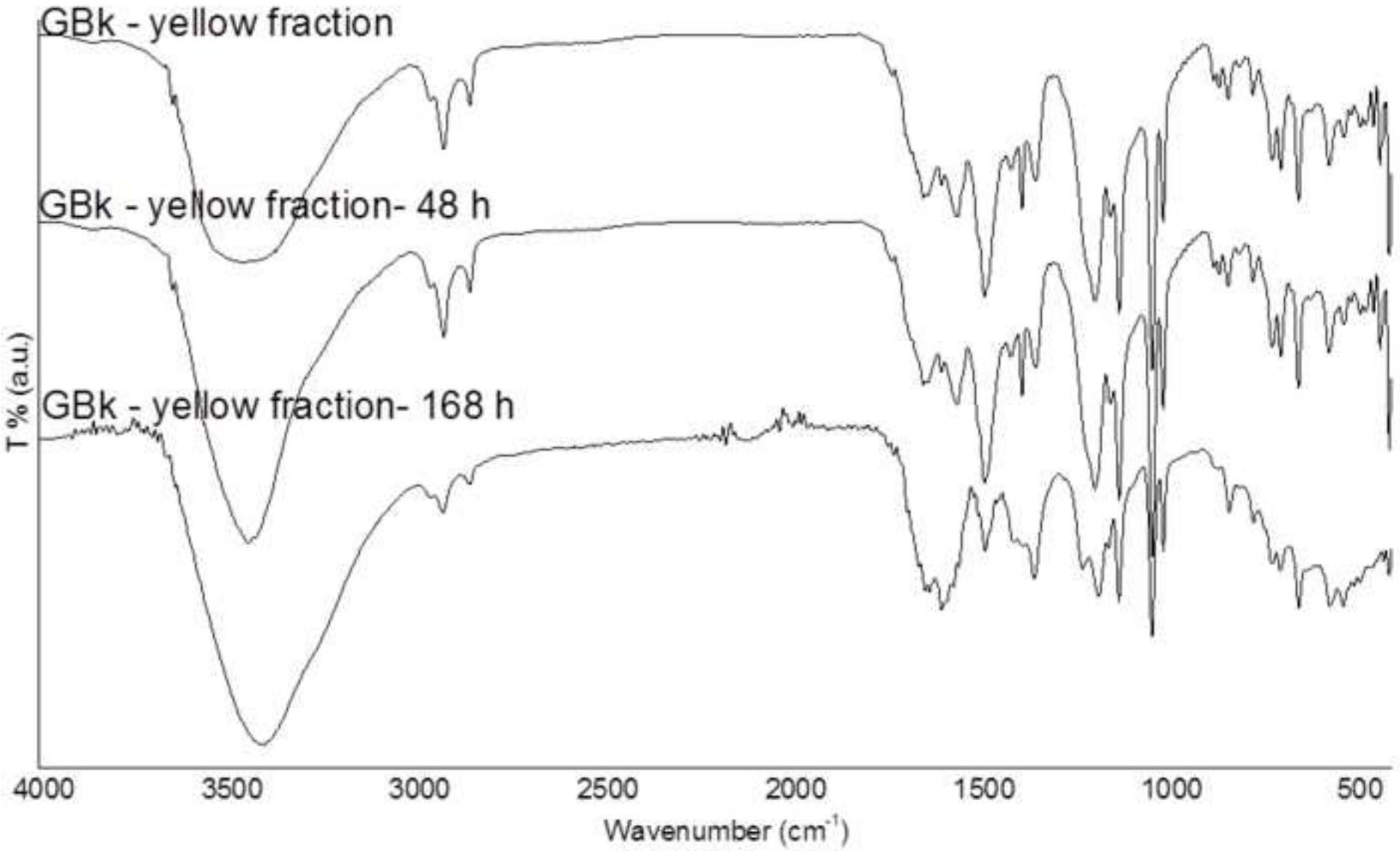

Captions for supplementary material

Figure a Infrared spectra of blue inks: SB, LB and GB ink

Figure b Infrared spectra of red inks: LR and GR ink

Figure c Infrared spectra of black inks: SBk and PBk ink

Figure d.1 Infrared spectra of blue fraction of sample GBk after 0, 48, 168 hours of lamp exposure.

Figure d.2 Enlargements in the range 2000-800 cm^{-1} of infrared spectra of blue fraction of sample GBk after 0, 48, 168 hours of lamp exposure. In the boxes: peaks enlightening changes in AB 9 structure.

Figure e Infrared spectra of red fraction of sample GBk after 0, 48, 168 hours of lamp exposure.

Figure f Infrared spectra of yellow fraction of sample GBk after 0, 48, 168 hours of lamp exposure.

Tables and captions

Table 1 : List of the analysed felt pen inks. Commercial information, colours and manufacturers are specified according to the producers' datasheet

Sample name	*Commercial name*	*Colour*	*Manufacturer*
SR	Stabilo Pen 68/48	Red	Stabilo, Germany
SB	Stabilo Pen 68/32	Blue	
SBk	Stabilo Pen 68/46	Black	
GR	Giotto Turbo color	Red	Giotto, Italy
GB	Giotto Turbo color	Blue	
GBk	Giotto Turbo color	Black	
LR	Lyra Hi-quality Art Pen 017	Red	Lyra, Italy
LB	Lyra Hi-quality Art Pen 050	Blue	
LBk	Lyra Hi-quality Art Pen 099	Black	
PR	Pentel S520B	Red	Pentel, Japan
PB	Pentel S520C	Blue	
PBk	Pentel S520A	Black	

Table 2: Summary of the identified compounds in the formulations of the analysed felt-tip pen inks

Samples	Dyes and Pigments*	Solvent/Additives**
SR	Acid Red 18 Acid Yellow 23	PEG, Glycerol, FA
SB	Pigment Blue 15:x *Quinoxaline-based pink dye (?)*	PEG, Glycerol, FA
SBk	Acid Red 18 Acid Blue 9 *Pigment Black 7 (?)*	PEG, Glycerol, FA
GR	Acid Red 18	DEG, FA
GB	Acid Blue 9	DEG, PEG, FA, Benzotriazole derivative
GBk	Acid Red 18 Acid Yellow 23 Acid Blue 9	DEG, FA
LR	Acid Red 18 Acid Yellow 23	DEG, 2-Phenoxyethanol, FA, Colophony
LB	Acid Blue 9	DEG, 2-Phenoxyethanol, FA, Colophony
LBk	Acid Red 18 Acid Yellow 23 Acid Blue 9 *Quinoxaline-based pink dye (?)*	DEG, 2-Phenoxyethanol, FA, Colophony
PR	Acid Red 87	Ethylene glycol, 2-Phenoxyethanol, FA, Benzotriazole derivative
PB	Acid Blue 9 *Quinoxaline-based pink dye (?)*	DEG, PEG, 2-Phenoxyethanol, FA, Benzotriazole derivative
PBk	Acid Blue 9 *Pigment Black 1 (?)* *Pigment Black 7 (?)*	Ethylene glycol, 2-Phenoxyethanol, FA, Benzotriazole derivative

* ***(?)= not confirmed***

** **DEG = diethylene glycol, PEG = polyethylene glycol, FA = fatty acids**

Table 3: Elemental composition of the formulations of the analysed felt-tip pen inks

Sample name	Element*					
	S	Ca	K	P	Br	Cu
SR	++	+	-	-		
SB	++	+		+		++
SBk	++	+		-		
GR	++	+	-	+		
GB	++	+		+		
GBk	++	+	-	-		
LR	++	+		+		
LB	++	+		+		
LBk	++	+		+		
PR	++	+		+	++	
PB	++	+		+		
PBk	++	+		-		

* ++ = very abundant, += abundant, -= traces

Table 4. Main FT-IR absorption bands of the identified dyes

	Assignment	OH, NH region 3700-3200 cm^{-1}	CH region 3200-2400 cm^{-1}	C=C, C=N, NH reg 1800 - 1550 cm^{-1}	Fingerprint region 1550 - 500 cm^{-1}
GBk- blue fraction	AB 9	3416	2984, 2928	1618, 1576	1409, 1391, 1340, 1190, 1171, 1141, 1117, 1075, 1040, 916, 730, 618
GBk- red fraction	AR 18	3416	2921, 2853	1626, 1571, 1541	1492, 1402, 1193, 1148, 1096, 1047, 981, 836, 753, 684, 658, 617, 594
GBk- yellow fraction	AY 23	3461	2921, 2852	1647, 1556	1484, 1384, 1348, 1191, 1126, 1038, 1009, 836, 718, 696, 649, 568
PR- pink fraction	AR 87	3444	293, 3853	1628, 1606, 1555	1503, 1465, 1386, 1354, 1270, 1239, 1090, 1058, 976, 723

Supplementary Materials (1)

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