

Non-destructive FT-IR analysis of mono azo dyes

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In this study, a scheme is developed for the systematic identification and classification of mono-azo dyes on the basis of infrared spectral analysis, to aid in the detection of functional groups of unknown mono-azo dyes, without using any toxic chemicals. This non-destructive and 'green' analytical method is applicable for dyes, and may also be applicable for dyed consumer products and goods, without any tedious sample preparation steps or reductive cleavage of azo bonds. Ten mono-azo dyes were synthesized in the laboratory from three different intermediates; anthranilic acid, sulfanilic acid and aniline and were subjected to FT-IR spectroscopy (with their respective precursor amines) to formulate a comparative analysis. The spectral bands due to azo bond, amines, aromatic region and other covalent bonds present in the mono-azo dye molecules in the obtained FT-IR spectra are discussed. The importance of the relative location of the azo band with respect to neighboring bands is also highlighted with their differentiation. Special emphasis is given on the identification of azo and aromatic region in the FT-IR spectra, which could be helpful in resolving confusions often confronted in azo dye detection. The study also explains drifted azo bands in the spectra and the possible reasons behind them. The results and the scheme were validated with spectral examples of pure mono-azo and non-azo dyes.

Keywords: mono-azo dyes, FT-IR spectroscopy, characterization, non-destructive, azo detection

INTRODUCTION

The Fourier transform infrared (FT-IR) spectroscopy is an important physical technique among other techniques such as mass spectrometry, UV, UV-visible and NMR spectroscopy, etc. FT-IR spectroscopy is used to study the functional groups present in molecules and for the characterization of covalent bonds within the molecules. FT-IR spectroscopy is a non-destructive, fast and sensitive physical technique for the analysis of organic compounds with minimum sample preparation [1]. It can serve as a fingerprint technique for the classification of unknown compounds, therefore it is very helpful in classifying raw materials and ingredients that are used in dyes, paints, polymers, plastics, coatings, laminates, pharmaceuticals, foods and other consumer products. It is also useful for the structural elucidation and confirmation of known and novel natural organic compounds/products isolated from terrestrial plants [2] and algae [3] with the aid of other physical techniques such as mass spectrometry, UV, UV-visible and NMR spectroscopy. FT-IR spectroscopy is also used in the analysis of fats and oils and it can also be associated with 'green analytical chemistry' because this technique reduces the use of chemical reagents hazardous to the environment and human health [4]. FT-IR spectroscopy is widely used as a

powerful analytical tool in oil & food research to qualitatively and quantitatively analyze specific organic food components in combination with certain chemometric packages [5].

Nowadays, new environmental issues are emerging and there are more concerns on the ecological use of safe and environment friendly chemicals in consumer goods and products. Dyes are widely used in most of the consumable products such as textile, leather, soft drinks, candies, paints, plastics, pharmaceuticals, etc., to attract people and increase sales. As a result, it is very difficult to screen them all and some harmful azo dyes are still being used in consumer products which create health and environmental problems. Some azo dyes can be easily reduced under mild reducing conditions, (sometimes even with the help of some enzymes in the human body) splitting into forbidden aromatic amines such as benzidine, aniline and their derivatives, etc. [6, 7] so-called MAK amines, thus releasing toxic chemicals into the environment. Standard methods are available and have been adopted globally to determine the harmful aromatic amines in many of the consumer products. But a drawback in such methods is the use of chemical reagents which are hazardous to human health and environment. Some studies have been reported earlier for the characterization and comparison of dyes [8-11]. There are vast applications of infra-red spectroscopy for the successful analysis of ancient textile dyes [12],

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forensic analysis of dyestuffs and inks [13]. This scheme could even be exploited in the analysis of dyes within the matrix without extraction [13, 14]. In this study, the azo bonds and conjoined aromatic amines in the dye molecules have been speculated with the help of FT-IR spectroscopy, with simple and easy sample preparation, without any reductive cleavage of the azo bond and without using any harmful chemicals.

MATERIALS AND METHODS

The starting chemicals like α -naphthol, β -naphthol, aniline, and anthranilic acid (general purpose reagent) were supplied from BDH Ltd. Poole, England. Sulfanilic acid was obtained from Fluka. All other chemicals employed were of A.R. grade, unless mentioned.

The dyes (a to i, Table 1) were synthesized in-house by diazotization reaction [15]. *p*-Aminoazobenzene (a), *p*-aminoazobenzene hydrochloride (b), diazoaminobenzene (c), reddish brown (d) and reddish yellow (e) were synthesized from aniline, taken as a precursor amine. Food yellow 8 (f), bright reddish orange (g) and orange 1 (h) were synthesized from sulfanilic acid (precursor amine). lake red D (i) was synthesized from anthranilic acid (precursor amine). All mono-azo dyes were thoroughly ground by mortar and pestle until a fine powder was obtained. The powdered samples were analyzed on a FT-IR spectrophotometer, Nicolet Avatar 330 from Thermo Electron Corporation, equipped with Smart accessory. The prepared samples were applied on a zinc selenide (ZnSe) window and pressed with adequate pressure to form a thin film for analysis. The scan rate was set at 32 scans per spectrum at a spectral resolution of 2 cm^{-1} . The absorption bands and details of the mono-azo dyes used for spectral studies are given in Table 1.

RESULTS AND DISCUSSION

Spectral comparison of dyes with respective intermediates

In-house synthesized mono-azo dyes were confirmed through color development and verified with the help of FT-IR spectroscopic analysis. The spectra are presented in Figs 1 and 2, in a stacked view for comparison and truncated above 2000 cm^{-1} to focus on the targeted bands. The FT-IR spectra of dyes (a) to (i) (Table 1) show prominent azo bond (N=N) vibrations which are identifiable between 1504 cm^{-1} and 1555 cm^{-1} [Figs 1, 2 and 3] which can be clearly distinguished from the spectra of their respective intermediates (aniline,

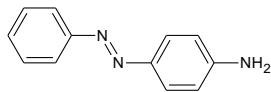
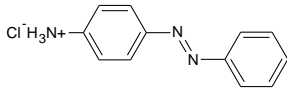
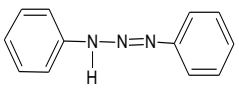
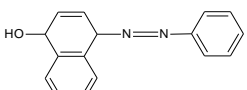
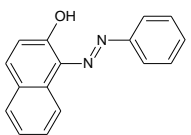
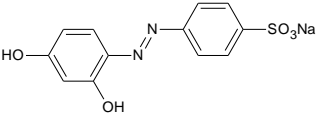
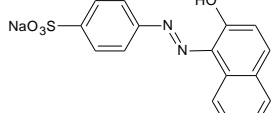
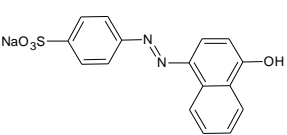
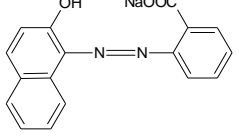
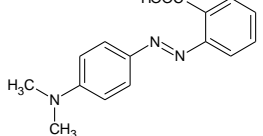
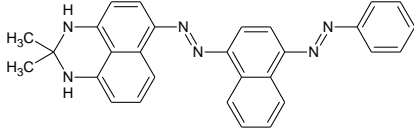
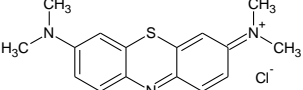
anthranilic acid and sulfanilic acid, *cf.* Table 2). The absorption frequency of sulfanilic acid due to aromatic ring occurs at 1573 cm^{-1} and 1498 cm^{-1} while C-N stretching occurs at 1240 cm^{-1} (Fig. 2). In case of anthranilic acid, the aromatic ring absorption appears at 1574 cm^{-1} and 1453 cm^{-1} and the C-N stretching at 1230 cm^{-1} (Fig. 2).

The C-N stretching is at 1281 cm^{-1} while the aromatic ring band is next to the N-H band in the IR spectrum of aniline (Fig. 1). Liquid aniline was not subjected to FT-IR spectroscopy, due to its toxicity. Its IR spectrum was downloaded from the National Institute of Science and Technology website; <http://webbook.nist.gov>.

Identification of mono-azo dyes through IR Spectra

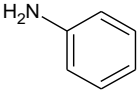
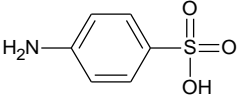
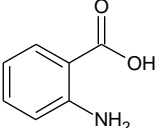
The main purpose of this study is to introduce a non-destructive method of using spectral information to identify mono-azo dyes, as an alternative way compared to the conventional analysis, after reductive cleavage of the azo bond. The analysis was carried out for lab synthesized dyes, therefore it is definitely valid for dyes in pure form. The significant bands are those due to the azo chromophore (-N=N-), C-N stretching and other bands, e.g. aromatic ring (Figure 3), etc. For this purpose the IR spectrum of pure methyl red (Merck) was recorded for comparison with the mono-azo dyes, synthesized in-house (Figure 2). The bands due to the aromatic region in the range of 1400-1600 cm^{-1} are also significant as azo bond stretching appears between the bands of the aromatic region (Figures 1, 2 and 3). The stretching of aromatic region is prominent and strong (Figures 1 and 2). The absorption band of the azo chromophore is clearly distinct from the C=C absorption bands which are quite evident in Figures 1, 2 and 3. The azo absorption bands in the various mono-azo dyes (a to i, Table 1) were sited between 1504 cm^{-1} and 1555 cm^{-1} . Due to aromatic region, the higher energy bands appeared from 1419 cm^{-1} to 1487 cm^{-1} while the lower energy bands ranged from 1590 cm^{-1} to 1619 cm^{-1} . The absorption of C-N is also discussed as supporting evidence and its frequency ranges from 1225 cm^{-1} to 1317 cm^{-1} . The C-N stretching in the IR spectrum of acid orange 20 appeared at 1317 cm^{-1} (Table 1 and Fig. 2), because resonance increases the bond order between the ring and the attached nitrogen atom (Figs. 1 and 3). Figures 1 and 2 were created with the help of software "Essential FTIR" (version 2.00.037).

Table 1. Key absorption bands and structures of mono-azo dyes.

| Dye identification with Molecular formula | Dye Code | Absorption Bands (cm ⁻¹) | Structures |
|---|----------|--|---|
| Solvent Yellow 1 (Sudan Yellow R) (C ₁₂ H ₁₁ N ₃) | (a) | 688 (s), 766 (s), 832 (s), 1137 (m), 1298 (br), 1311 (m), 1324 (m), 1411 (m), 1503 (m), 1594 (s), 1616 (m) |  |
| Solvent Yellow 1 (p-Aminoazobenzene hydrochloride) (C ₁₂ H ₁₁ N ₃ .HCl) | (b) | 680 (s), 700 (m), 747 (m), 798 (s), 852 (m), 1171 (s), 1262 (m), 1369 (s), 1453 (m), 1524 (m), 1544 (m), 1604 (m), 1614 (s), 1655 (s) |  |
| Triazene, 1,3-diphenyl (Benzeneazoaniline / p-diazoaminobenzene) (C ₁₂ H ₁₁ N ₃) | (c) | 688 (s), 749 (s), 1072, 1202 (m), 1254 (m), 1416 (s), 1464 (m), 1603 (m) |  |
| Solvent Brown 4 (Dull Reddish Brown) (C ₁₆ H ₁₂ ON ₂) | (d) | 687 (m), 742 (s), 759 (s), 809 (m), 835 (m), 881 (m), 1261 (s), 1324 (m), 1354 (m), 1417 (s), 1455 (s), 1480 (s), 1544 (s), 1599 (s), 1615 (w) |  |
| Solvent Yellow 14 (Sudan 1) (C ₁₆ H ₁₂ ON ₂) | (e) | 740 (s), 810 (s), 845 (m), 1167 (m), 215 (m), 1276 (m), 1468 (m), 516 (m), 1599 (m), 1629 (m) |  |
| Acid Orange 6 (Food Yellow 8) (C ₁₂ H ₉ O ₅ N ₂ Na) | (f) | 650 (s), 722 (s), 824 (m), 849 (m), 1032 (s), 1117 (s), 1163 (s), 1227 (s), 1369 (m), 1418 (m), 1507 (w), 1592 (m), 1630 (m) |  |
| Acid Orange 7 (Bright Reddish Orange) (C ₁₆ H ₁₁ O ₄ N ₂ SNa) | (g) | 692 (m), 753 (s), 836 (s), 1032 (s), 1115 (s), 1185 (s), 1228 (m), 1446 (w), 1503 (m, br), 1555 (w), 1594 (w), 1625 (w) |  |
| Acid Orange 20 (Orange I) (C ₁₆ H ₁₁ O ₄ N ₂ SNa) | (h) | 702 (s), 758 (s), 832 (m), 1123 (s), 1186 (s), 1317 (m), 1519 (m), 1541 (m), 1604 (m), 1634 (s) |  |
| Pigment Red 50 (Lake Red D) (C ₁₇ H ₁₁ O ₃ N ₂ Na) | (i) | 740 (s), 749 (s), 827 (m), 849 (m), 1211 (w), 1250 (w), 1372 (s), 1390 (s), 1437 (s), 1477 (m), 1551 (w), 1594 (m), 1616 (m) |  |
| Acid Red 2 (Methyl Red) (C ₁₅ H ₁₅ N ₃ O ₂) | (j) | 1593(s) 1601 (s), 1366 (s), 1273 (s), 1144 (s), 1111 (s), 818 (s), 764 (m) |  |
| Solvent Black 3 (Sudan Black B) (C ₂₉ H ₂₄ N ₆) | (k) | 1594 (s), 1290 (m), 1214 (m), 1166 (m), 1129 (s), 1003 (w), 118 (s), 759 (s), 688 (m) |  |
| Basic Blue 9 (Methylene Blue) (C ₁₆ H ₁₈ N ₃ SCl) | (l) | 1595 (s), 1487 (m), 1390 (s), 1328 (s), 1128 (m), 816 (s) |  |

Key: w = weak, s = strong, m = medium, br = broad

Table.2. Key absorption bands and structures of dye intermediates.

| Dye Intermediates with Molecular Formula | Absorption Bands (cm ⁻¹) | Structures |
|--|---|---|
| Aniline (C ₆ H ₅ NH ₂) | 1281 |  |
| Sulfanilic Acid (C ₆ H ₇ NO ₃ S) | 1240 (w), 1154 (s), 1111 (s), 1033 (s), 1008 (m), 829 (m) |  |
| Anthranilic Acid (C ₇ H ₇ NO ₂) | 1659 (w), 1574 (m), 1276 (m), 1230 (m), 764 (s), 834 (m) |  |

Key: w = weak, s = strong, m = medium

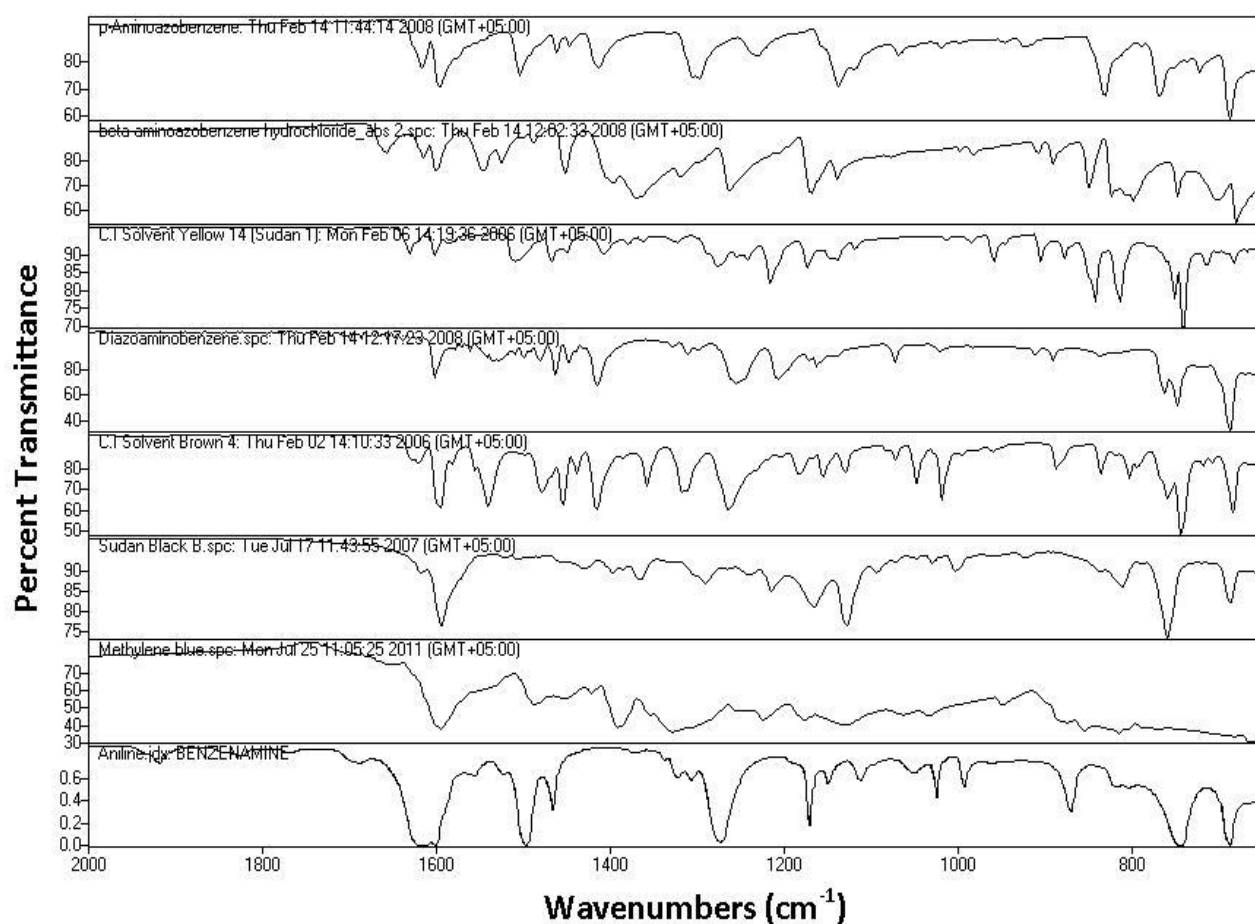


Fig. 1. IR spectra of aniline, methylene blue, sudan black b, solvent brown 4, diazoaminobenzene, solvent yellow 14, *p*-aminoazobenzene hydrochloride, and *p*-aminoazobenzene (from bottom to top) respectively.

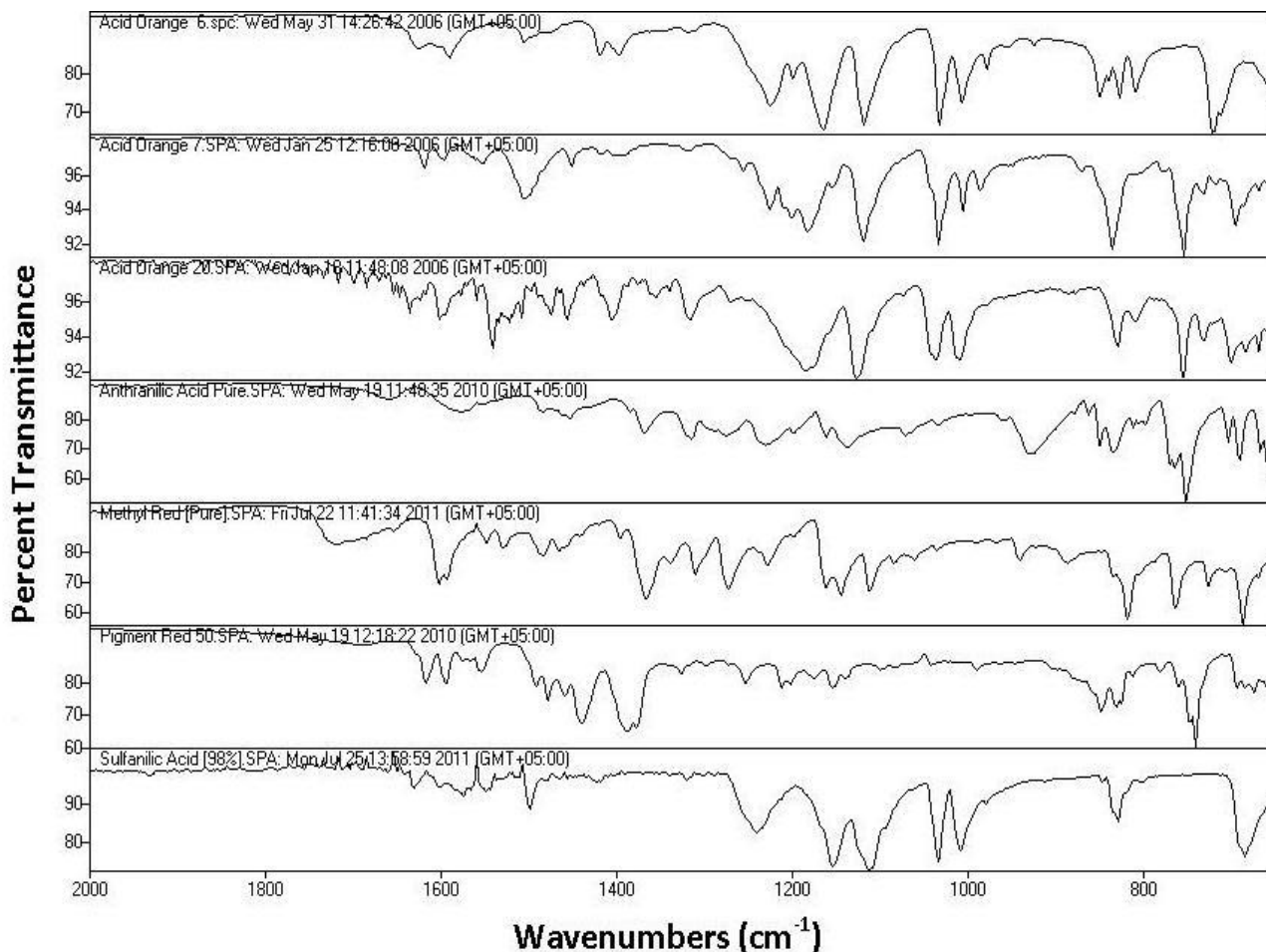


Fig. 2. IR spectra of sulfanilic acid, pigment red 50, methyl red, anthranilic acid, acid orange 20, acid orange 7 and acid orange 6 (from bottom to top), respectively

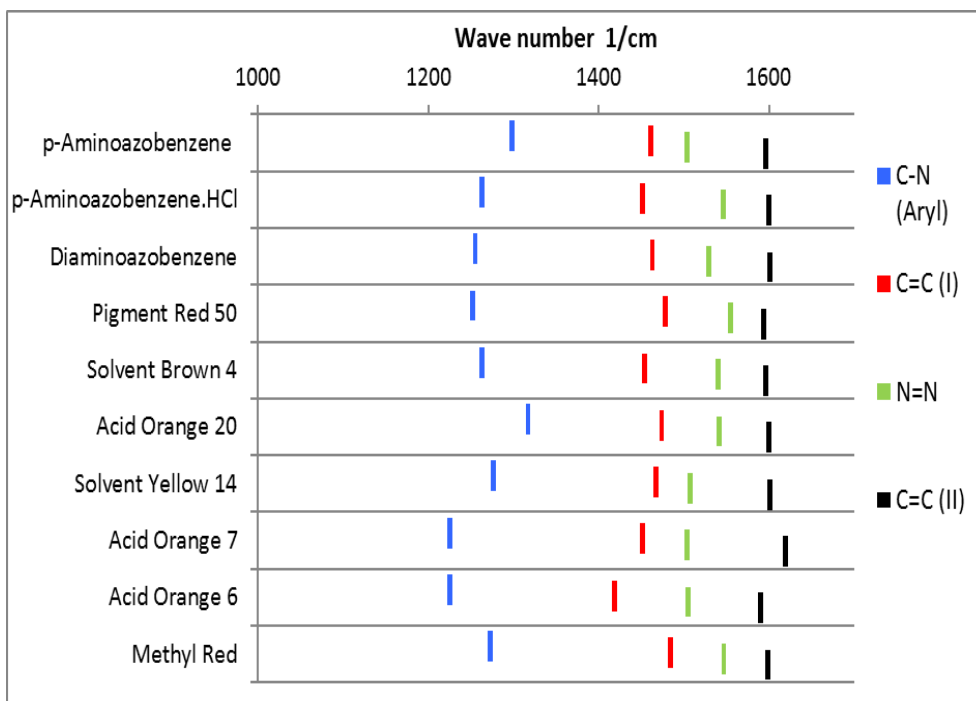


Fig. 3. Characteristic vibrations of different mono-azo dyes.

Methyl red

The aromatic region (C=C) appears in the spectrum at 1601 cm^{-1} and 1484 cm^{-1} . The 1528 cm^{-1} and 1547 cm^{-1} frequencies are due to azo chromophore. 1273 cm^{-1} is due to C-N stretching (azo bond C-N). The C-N absorption occurs at a higher frequency in aromatic compounds because resonance increases the double bond character between the ring and the attached nitrogen atom [15]. The C-N stretching for tertiary amine appeared at 1162 cm^{-1} and 1144 cm^{-1} .

Methylene blue

The spectrum of methylene blue (non azo dye) was included in the study for the sole purpose of comparison with the spectra of mono-azo dyes in general. The first and marked difference is the complete absence of the azo stretching band in the methylene blue IR spectrum (Fig. 1).

It is possible that the presence of some functional groups like $-\text{CH}_2-$ (1465 cm^{-1}) and $-\text{CH}_3$ (1450 cm^{-1}) could interfere in the spectral interpretation and band identification. In such cases additional examination is necessary.

Spectral comparison of mono-azo and bis-azo dye

Figures 1 and 2 contain the spectra of sudan black B (bis-azo) and methyl red, stacked for the convenience of comparison. The band for the azo chromophore is small as compared with those in other mono-azo dyes, because of the larger number of C=C bonds (i.e. a richer aromatic region) in sudan black B. The N=N band may also have increased because of an extra azo chromophore, but not in comparison with the C=C bonds. The aromatic region peaks in the spectrum of sudan black B appear at 1594 cm^{-1} and 1430 cm^{-1} . The band due to azo is 1521 cm^{-1} and 1505 cm^{-1} and the CN band is at 1290 cm^{-1} [17, 18, 19].

CONCLUSIONS

The spectral interpretation of dye spectra revealed valuable information about the identification and characterization of mono-azo dyes without any reductive cleavage of azo bond present in the dyes, for the attraction of buyer, especially in the analysis of dyes which are used in consumer products and goods. The key identification, the azo band region was found to appear between 1504 cm^{-1} and 1555 cm^{-1} . Detailed analysis revealed that the azo and the aromatic region bands drifted in some cases, while in other cases the azo bands appeared separate and distinct.

The technique is non-destructive, fast and very useful even for small sample quantities. The study is a prelude for bright possibilities of azo identification without any need for the separation of dyes from their matrices. These findings are crucial for the monitoring of azo dyes in consumer products and goods where environmentally friendly dyes should be used.

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НЕ-ДЕСТРУКТИВЕН FT-IR АНАЛИЗ НА МОНО-АЗОБАГРИЛА

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(Резюме)

Създадена е схема за системна идентификация и класификация на моно-азобагрила на базата на инфрачервен спектроскопски анализ за откриването на функционални групи в неизвестни моно-азобагрила без употребата на токсични химикали. Този не-деструктивен и „зелен“ аналитичен метод е приложим за багрила и може да бъде приложен за багрени продукти и стоки без предварителното редукиционно разкъсване на азо-връзката. Десет моно-азобагрила бяха синтезирани от три различни междинни съединения: антрапилово киселина, сулфанилово киселина и анилин и бяха изследвани с FT-IR спектроскопия (заедно с техните прекурсори-амини) за формулиране на сравнителен анализ. Обсъдени са спектралните линии на азо-връзките, амините, ароматната област и други ковалентни възки в молекулите на азобагрилата. Значението на относителната локализация на азо-линиите по отношение на съседните линии също е обяснено с тяхната диференциация. Специално внимание е обърнато на идентификацията на азо- и ароматните области в FT-IR спектрите, което може да е полезно за решаване на недоразумения при откриването на азобагрила. Тези резултати и приложената схема са потвърдени за примери от чисти азо- и други багрила.