Development and certification of reference materials for the determination of aromatic amines in textile matrices

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***Abstract*—In this work, new reference materials are developed for the identification of forbidden aromatic amines used in the synthesis of azo dyes for the textile industry. In this perspective, after a theoretical study on these materials and on the quality control in the textile industry, we synthesized azo dyes based on forbidden amines which are then grafted on a textile matrix to elaborate the envisaged reference materials. Finally, we studied the different parameters that influence the properties of these materials.**

Keywords—Certified reference material, Azo dyes, Textile, Aromatic amines formatting.

I. INTRODUCTION

Dyes have always been part of human life; they are present in many industrial applications around the world. Indeed, on the various sites of ancient and antique civilizations, colors were extracted from natural sources, either of vegetable origin (beets, flowers...), or of animal origin (cochineal, shells, ...) [1]–[3]. Then thanks to the progress of the industrial world, the development of synthetic dyes is based on the identification of functional groups of molecules responsible for the absorption of electromagnetic energy in the visible range (~400-800 nm) that give rise to the color. Synthetic dyes can be classified into two broad categories: non-azo dyes and azo dyes [4], [5]. Indeed, azo dyes represent the greatest amount of production in dye chemistry today, and there is potential for their further increase in future relative importance[6], [7].

The azo are the compounds constituted by the functional group azo (-N=N-) uniting two identical or not alkyl or aryl groups (symmetrical and dissymmetrical azo). These structures which are generally based on the skeleton of the azo structure (azobenzene) are aromatic systems linked by an azo (-N=N-) chromophore group, and the fact of introducing for example azo groups between two aromatic rings shifts the absorption spectrum of benzene towards the long wavelengths so that the color appears (bathochromic effect) [8], [9].

Azo dyes are the most important synthetic dyes that have been widely used in textiles [10], however, they have harmful effects on humans and environment [11], they are characterized by a chemical group capable of forming covalent bonds with textile substrates, in fact a textile article dyed with a poorly fixed risky dye has low dye fastnesses [12]. This can lead to a bleeding of the dye on the skin in case of perspiration, which leads to the breaking of the azo chemical bond by the intervention of azoreductases (dye-degrading enzymes), the aromatic amine thus released is assimilated by the organism and concentrates in the bladder and consequently causes a risk of cancer [11]. As a result, the use of these amines is now governed in many countries by national and international regulations (e.g., ISO 14362-2) that have banned the use of certain aromatic amines considered to be carcinogenic .

Therefore, analytical methods for the precise determination of these amines are needed to implement these regulations. Indeed, focusing on the chemical analysis of toxic pollutants in textile matrices, especially azo dyes. It is rare to find a specific database or catalog for the determination of these pollutants in textile matrices. In this regard, certified reference materials (CRMs) are one of the most preferred tools. However, these CRMs containing toxic pollutants are difficult to find, and participation in interlaboratory testing campaigns, when they exist, is very expensive, hence the need to develop and certify reference materials in the textile field.

In this respect, the aim of our study is to develop a new reference material for textiles. This new material is in the form of a fabric which essentially contains azo dyes synthesized from prohibited amines. These dyes must be incorporated into the fabric in a homogeneous way. To achieve this aim, we have synthesized and characterized six azo dyes based on six prohibited amines. These dyes will be then grafted in a homogeneous way on a textile matrix via the dyeing.

II. MATERIALS AND METHODS

A. Materials

The chloridric acid (HCl) (37 %), sodium nitrite (NaNO3) (99%), beta-naphthol (99 %), Sodium hydroxide (NaOH) (99%), dispersing agent (99 %), and unison agent (99 %), and various amines (4 chloraniline ; O -anisidine ; 4,4' oxydianiline ; O-toluidine and 6-méthoxy- m -toluidine) (99%) (see table I) were purchased from Sigma-Aldrich Co. No further purification was done to the reagents, with deionized water used as a solvent.

B. Azo dye synthesis

The synthesis of an azo dye is done in two steps: The diazotization and the coupling (see Figure 1). Indeed, during the step of diazotization the aromatic amines form in the presence of nitrous acid and chloridric acid the diazonium salt. During the coupling step the diazonium salt formed is reacted with b-naphthol in the presence of NaOH to form the azo dye.

Thus amine, chloridric acid (HCl) and water are mixed, the first solution being obtained, sodium nitrite (NaNO3) is dissolved in water forming the second solution. then, beta-naphthol is dissolved in 10% NaOH. The solution obtained is designated as solution 3 The three solutions are placed separately in an ice-filled crystallizer until they reach a temperature of 0-5°C. Then, solution 2 is added to solution 1 to obtain a solution which is then poured with the help of a capillary on solution 3 of beta-naphthol, the whole is maintained under agitation until obtaining a foam which is filtered then put under vacuum and washed with water and finally recovered in the form of solid dye.

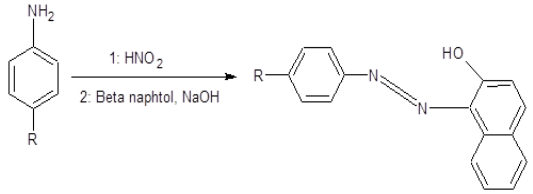
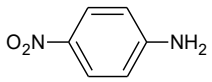
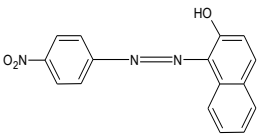
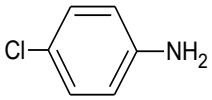
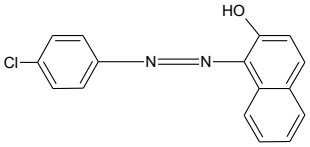
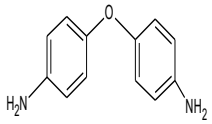
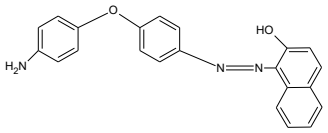
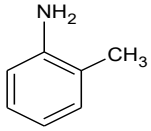
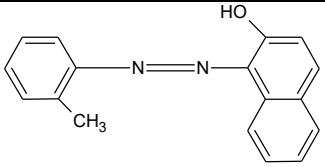
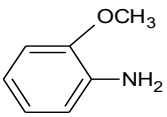
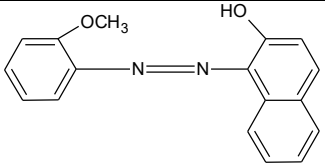
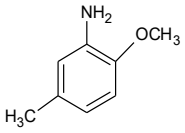
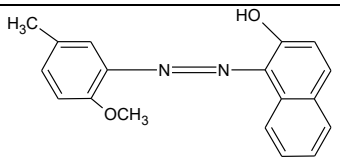


Figure 1 : Reaction of the azo dyes synthesis.

TABLE I. THE DIFFERENT AMINE USED AND THE SYNTHESIZED DYES

N	Amines	Dyes	Name
1			p-Nitroaniline
2			p-Chloroaniline
3			4,4-Oxydianiline
4			o-Toluidine
5			o-Anisidine

6			p-Crésidine

C. Reference material preparation

1) Choice of the textile matrix

The dyes that we have synthesized do not contain reactive groups that form covalent bonds with the cotton fiber. Moreover, they are insoluble in water which prevents their diffusion in the fiber. On the other hand, in the case of polyester, these insoluble dyes are easily incorporated into the fiber at high temperatures. Indeed, the dyeing of polyester is generally carried out between 130 and 140 °C. With the increase of the temperature the solubility of the dye increases especially above 100 °C. At 130 °C the oscillation of the macromolecular chains becomes very important which increases the free volume, and the dye starts to diffuse in the fiber. For these reasons, we have chosen polyester as matrix in this work.

2) Dyeing of polyester

The polyester fabrics were dyed at high temperature. At first, we applied the general process of dyeing. Then we studied the influence of the solubility of the dyes and the temperature of the process on the homogeneity of the dyeing. Finally, we have made different shades to draw the correlation curve between the concentration of the amine remained on the fabric and the percentage of dye with which we dyed the polyester fabrics.

3) Study of the dye solubility

In order to study the influence of dye solubility on dye homogeneity, we prepared a dye bath with different percentage of dye, a dispersing agent (1,5g/l), and a unison agent (0,5g/l), for a bath ratio of 1:10 and 5 g of polyester fabric (see table II).then we launched the dyeing without previous solubilization of the dye according to the procedure illustrated in figure 2.

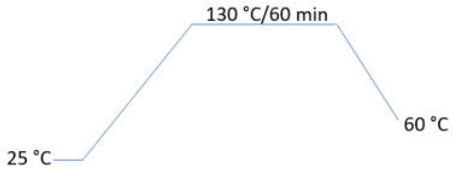


Figure 2 : General dyeing process 1.

4) Study of the temperature influence on the dye homogeneity

To study the influence of temperature on the homogeneity of the dyeing process, a step at 110 °C for 15 min was added to process 1 (figure 3) ,to allow the dye to disperse better on the surface of the fabric (see table II).

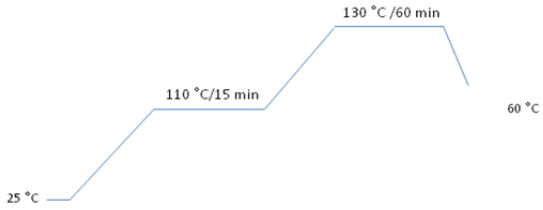


Figure 3 : process 2 of the optimal dyeing conditions

TABLE II. TEST SAMPLES FOR THE STUDY OF THE DYE SOLUBILITY AND HOMOGENEITY.

Test	% of dye	Bath volume (ml)	Temperature range (°C)	Homogénéité
1	5	50	130	-
2	10	50	130	-
3	5	50	130	-
4	10	50	110-130	+
5	5	50	110-130	+

5) Study of the temperature influence on the dye homogeneity

In order to have different range of shades on the fabrics, we made different dyeing by varying the percentage of dyes from 2, 5, 10 to 15%, and we launched the dyeing according to the process 2 (see table III).

TABLE III. TEST SAMPLES FOR THE STUDY OF COLOR SHADE

Test	% of dye	Bath volume (ml)	Temperature range (°C)	Homogénéité
6	2	50	110-130	+
7	5	50	110-130	+
8	10	50	110-130	+
9	15	50	110-130	+

D. Characterization

The characterization of the synthesized dyes was carried out using a UV-vis spectrophotometer Thermo-Scientific Evolution 300. And the recording of FTIR spectra of the studied samples were realized using Nicolet iS10 FTIR-ATR spectrophotometer combined with the golden gate single attenuated total reflection (ATR) accessory. The range of experiments took place between 4000 and 400 cm-1 with a 4 cm-1 resolution along with an accumulation of 32 scans. [13] examined the development and refinement of possible mathematical models for the intellectual system of career guidance. Mathematical modeling of knowledge expression in the career guidance system, Combined method of eliminating uncertainties, Chris-Naylor method in the expert information system of career guidance, Shortliff and

Buchanan model in the expert information system of career guidance and DempsterSchafer in the expert information system of career guidance method has been studied. [14] discussed that Liver tumor division in restorative pictures has been generally considered as of late, of which the Level set models show an uncommon potential with the advantage of overall optima and functional effectiveness. The Gaussian mixture model (GMM) and Expected Maximization for liver tumor division are introduced. In the early liver division process Level set models are utilized.

III. Results and Discussion

A. UV-vis

According to figure 4 that shows the absorbance spectra of the synthesized dyes in methanol, we noticed that all the dyes absorb in the same wavelengths between 320-350nm except for the dye based on para-nitroaniline which absorbs at 400 nm. This deviation towards the longer wavelengths is due to the bathochromic effect of the nitro group (NO2) which is an electron attractor.

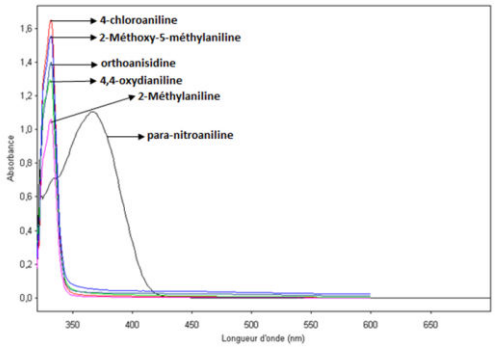


Figure 4 : UV-visible spectra of synthesized dyes in methanol

B. FTIR

The IR spectra of the synthesized dyes present bands of vibration of the group (C=O) are in 1600_1650 cm-1 range, There is a band between 3300 cm1 and 3500 cm-1, it characterizes the vibration of group (N_ H) and of the vibration of the alcohol function (O_H), thus vibration bands of (C=C) towards 1600cm-1, vibration bands of the group (C-O) located between 1000 cm -1 and 1300 cm -1. For the aromatic vibration bands there is (C-N) located between 1080 and 1360- cm -1, with (C_C) in 1585-1600 cm-1 range, the vibration band of aromatic H observed towards 3050 cm -1. For the compounds contains the chlorine atom presents a band of vibration around 750 cm -1, moreover in the spectrum is observed, the band of vibration of grouping (C_NO2) is around 1520cm -1, and the band of vibration of the function (N=O) appears between 1500cm -1 and 1600cm -1.

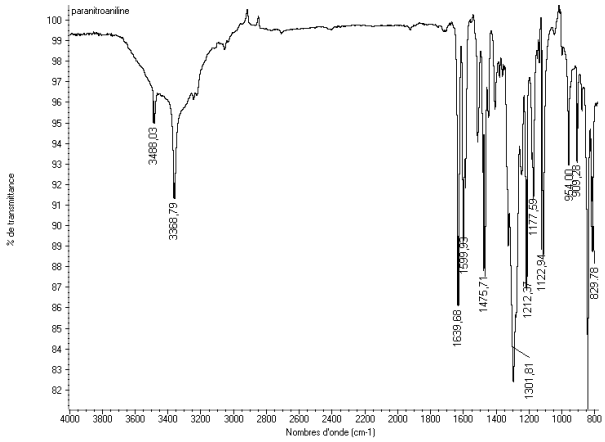


Figure 5 : infrared spectra of the synthesized dye 1

C. dye solubility

According to figure 6, the fabrics we obtained are stained by the dye, this may be due to the non-solubilization of the dye before launching the dyeing (test 1 and 2). However, to overcome this problem we solubilized the dye at 110 °C for 15 min before introducing the fabric and then we launched the dyeing according to process 1 (test 3), we found that even with the solubilization of the dye the stains remained on the fabric. For this reason, we thought to study another parameter that influences the homogeneity of the dyes which is the temperature.

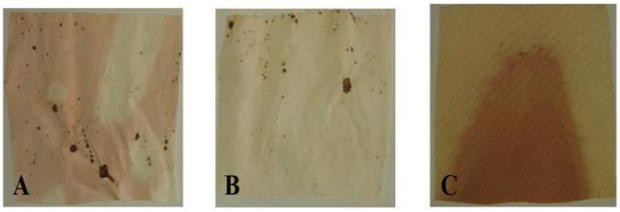


Figure 6 : Results obtained after washing and drying the samples of dye solubility study: A : Test 1; B : Test 2, C : Test 3.

D. Dye homogeneity

The addition of another temperature step to Process 1 revealed the influence of temperature on the homogeneity of the dyeing process, allowing the dye to better disperse on the fabric surface. The results obtained by applying process 2 (Test 4 and 5) are presented in Figure 7. These results allowed us to conclude that the added step is essential to have a good homogeneity of the dye.

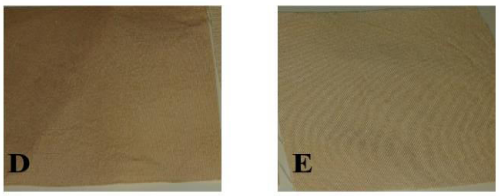


Figure 7 Results obtained after washing and drying the samples of dye homogeneity study : D: Test 4; E : Test 5.

E. Color shade

The study of the dyes on the tissues was successfully carried out with different dyes by varying their percentages and using process 2. The fabrics obtained are presented in figure 8, this study allowed us to see that the higher the percentage of dye, the darker the color becomes

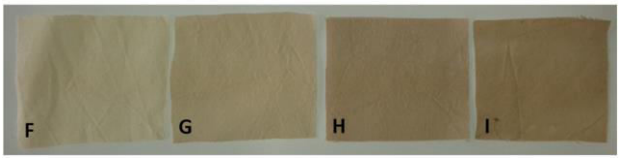


Figure 8 : Results obtained after washing and drying the samples of color shade study : F: Test 6; G : Test 7, H: Test 8; I : Test 9, I: Test 10.

IV. CONCLUSION

The requirements for reference material certification have evolved considerably in recent years with the demands of emerging industries where multiple analytes exist in a wide variety of matrices. The production of CRMs is a skill and need based activity that requires lengthy development before it can be brought to market. In this study, we succeeded in developing new reference materials for the identification of banned aromatic amines used in the synthesis of azo dyes for the textile industry. The encouraging results obtained gave us several perspectives and opened the way to the industrialization of the production of CRMs, to the development of new CRMs for other pollutants and for other matrices

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