

Rapid Screening Methods to Detect Banned Azo Dyes in Textiles

Lili Sun^{1,2*}, Zhenxing Lan¹, Xia Liu¹ and Fangfang Zuo¹

¹Guangzhou Inspection Testing and Certification Group Co., Ltd., China

²Guangdong Key Laboratory of Environmental Pollution and Health, School of Environment, China



Abstract

The detection of carcinogenic aromatic amines from banned azo dyes is one of routine test items in the third-party inspection agency. Due to the quantity of positive samples is less than 1% in recent years, it is meaningful to develop rapid screening methods to filter out the negative samples. This review summarizes the progress of rapid screening methods, which includes the rapid extraction technology and the chromogenic reactions instead of instrumental detection. With these rapid screening methods, it will save a lot of time and extraction reagent compared with the standard detection method. Furthermore, prospects for further study in the current research field are also discussed in this review.

Introduction

Azo dyes are widely used as synthetic organic colorants in textile industries [1]. Some kinds of azo dyes are banned as they could be reduced to aromatic amines through the biotransformation process [2]. Some kinds of aromatic amines are possibly absorbed by the skin, which can cause cancers. The European Union has classified 22 kinds of aromatic amines derived from azo dyes as potential carcinogens [3]. Both the European Union and China drew up related regulations about the limit value of these cancerogenic aromatic amines. The threshold of carcinogenic aromatic amines is not more than 30mg/kg in Annex XVII of the EU Chemical Regulation (EC/1907/2006) [4,5]. The threshold of carcinogenic aromatic amines is not more than 20mg/kg in the national general safety technical code for textile products in China (GB 18401-2011) [6].

The standard EN ISO 14362-1:2017 and GB/T 17592-2011 are usually used to test aromatic amines in textiles for the third-party inspection agency [7,8]. Generally, the determination involves a four-step process: sample pretreatment, reductive cleavage of azo bond, extraction of aromatic amines and instrumental determination. Large and precise instruments such as gas chromatography with mass spectrometry (GC-MS) or high-performance liquid chromatography (HPLC) are necessary for the instrumental determination [9]. Although the results are reliable, the testing process is time-consuming and costs high. Therefore, the rapid screening methods to simplify the extraction process and replace the instrumental determination are highly needed.

Rapid Screening Methods

The rapid screening method is recommended in the appendix of EN 14362-1:2017, in which the important simplification step is to use liquid/liquid shake extraction instead of column extraction. The expensive extraction solvent is reduced from 80mL to about 3mL [7]. In recent years, the chromogenic reactions of aromatic amines to replace the instrumental test have been used as qualitative methods to screen the aromatic amines (Figure 1). Two kinds of chromogenic reactions have been tried to the detection of carcinogenic aromatic amines in textiles. One is based on the diazotization coupling reaction mechanism of aromatic amines [10]. NaNO₂, ammonium sulfamate and o-methoxy-phenol are added one by one after the reduction and extraction of the textile samples. The results showed that the detection

***Corresponding author:** Lili Sun, Guangzhou Inspection Testing and Certification Group Co., Ltd., Guangdong Key Laboratory of Environmental Pollution and Health, School of Environment, China

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limit of the method was less than 15mg/kg. Comparing with the standard testing means, the advantage of this method is that the testing time is shortened by more than 60%, the reagent costs is saved more than 90%, and the whole test procedure could be processed without any chromatographic equipment. However, this method needs 4 kinds of reagents and about 15min to accomplish the chromogenic reactions. The other one is based on the mechanism of 4-dimethylaminobenzaldehyde with aromatic amines (Figure 2); [11]. This method only uses one kind of chromogenic reagent, and the chromogenic reaction can be accomplished within 1min. The results showed that the detection limit of the method was less than 15mg/kg.

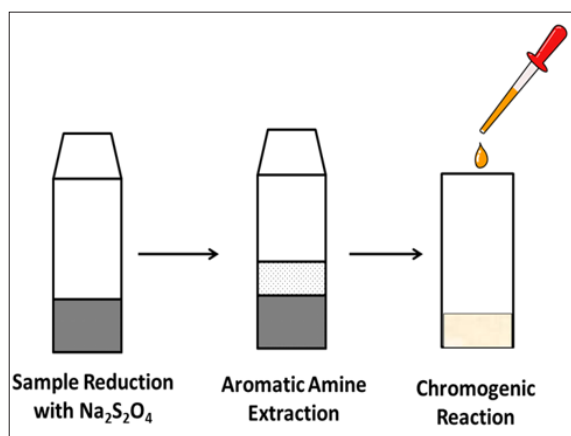


Figure 1: The steps for chromogenic reactions of aromatic amines.

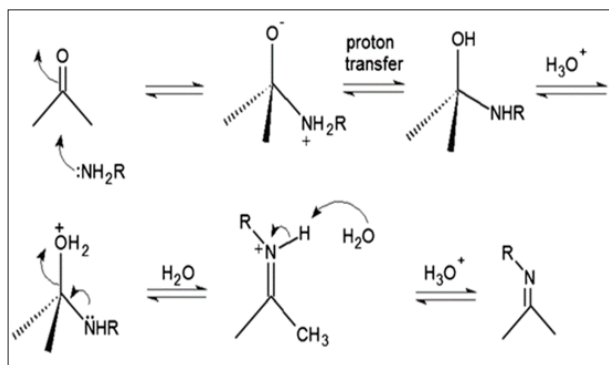


Figure 2: Reaction mechanism between a primary amine and an aldehyde or ketone [11].

Conclusion and Prospect

Taking account that the proportion of positive samples in recent years is less than 1%, it will save a lot of time and reagents by rapid chromogenic method based on the reactions of 4-dimethylaminobenzaldehyde with aromatic amines. Compared with the instrumental testing method, the rapid chromogenic method is suitable to be popularized and applied in the textile industries. For the future study, the quantitative method should be further developed using the ultraviolet-visible absorption

spectrometry in combination with chromogenic reactions. It will be a novel quantitative method to detect aromatic amines in textiles.

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