ABSTRACT

DETERMINING THE POTENCIAL OF CHROMATOGRAPHIC TECHNIQUES FOR THE IDENTIFICATION OF TEXTILE FIBERS TREATED BY SELECTED DESTRUCTIVE AGENTS FOR FORENSIC PURPOSES

The main goal of the doctoral dissertation was determining the potential of chromatographic techniques to identify of textile fibers treated by disinfectant, sterilizing and degrading DNA agents for forensic purpose. The carried out researches and the obtained results allowed to realize all of research goals.

During the experiments two types of fibers were tested: natural – cotton dyed with reactive dyes and synthetic – polyester fibers dyed with disperse dyes. Incidin, Domestos, Sterinox and Quatovet were the disinfectant agents, Cidex – the sterilizing agent and DNA Away – the DNA degrading agent. It was planned to determine the changes of textile samples treated by various destructive agents and to establish if chromatographic techniques (HPLC-DAD, UPLC-QTOF-MS) are useful tools for the analysis of fibers. The utility of the proposed chromatographic approach was compared with the results of macroscopic, microscopic and spectroscopic researches.

The first step of the research was focusing on cotton dyed with reactive dyes and eight reactive dyes as powders. Three chromatographic methods were tested: two from the literature and one which was developed for disperse dyes [110]. The methods descripted by Hoy et. al [57] and Schotman et. al. [22] allowed to identify respectively: four and six from the eight reactive dyes. Most of the observed signals were of low intensity. The method developed for disperse dyes was unsuitable for identifying reactive dyes. Optimization of Hoy's method [22] based on time extension from 5 min to 15 min and modification of gradient program allowed to identify all reactive dyes. At the same time UPLC-QTOF-MS method was being developed for reactive dyes. Unfortunately, the problems with ionization of these substances in ESI ion source caused this method to be ineffective for this purpose.

Extraction of dyes from cotton requires breaking the strong covalence bond between reactive dye and cotton fiber. It is related to obtaining the extracts of hydrolysed forms of reactive dyes. It means that the standards for chromatographic analysis should be hydrolysed forms of reactive dyes. The next goal of research was to establish the conditions for alkaline hydrolysis of reactive dyes. Previously, different variants of alkaline hydrolysis were tested for Reactive Red PD-3B

(8C). The most optimal conditions were to use the temperature of 100°C for 60 min and the molar ratio reactive dye to sodium hydroxide 1:1. The progress of reaction was monitored by thin-layer chromatography (TLC). Four different mixtures were used as the developing systems. Among them, the best one was a mixture of n-butanole:ethanole:ammonia:pyridine:water (6:3:2:6:6, v/v/v/v/v). The developed conditions allowed to obtain hydrolysed forms of all the reactive dyes.

The next step of these investigations was to apply the optimized alkaline conditions for the extraction of reactive dyes from 5 mm cotton threads. The obtained extracts were analyzed using an optimized HPLC-DAD method. Identification of reactive dyes was difficult to perform due to a lot of background signals (other compounds present in reactive dyes and other compounds generated from these dyes as a result of the alkaline hydrolysis reaction). However, the recorded chromatograms were different so they can be used as a valuable clue during a comparative analysis of materials collected at a crime scene e.g. from the criminal's clothes. The chromatograms recorded from 5 mm cotton threads treated by degrading agents were richer (many signals). Although, the qualitative analysis of the reactive dyes was difficult to perform, a characteristic chromatogram obtained for each tested sample can be a valuable piece of evidence during forensic analysis.

In the next stages of the investigations the macroscopic, microscopic and infrared spectroscopic analyses were performed in order to determine what kind of changes had occurred in cotton textiles treated by destructive agents. The research samples were cotton textiles and fibers degraded by selected agents. The obtained results showed that the greatest physicochemical changes were caused by Domestos. This agent discolored the cotton. Cotton fibers became brittle, frayed, in the form of short fragments, but the appearance of a flat ribbon with a characteristic twist was preserved. However, changes in the fluorescent properties were observed for all cotton fibers treated with other agents, i.e. DNA Away, Domestos, Cidex, Sterinox and Quatovet.

The infrared spectra obtained using the ATR technique (ATR-FTIR) in most cases were similar to the spectrum of undyed, non-degraded cotton. Only two agents: Domestos and Quatovet, drastically changed the spectra of the tested samples. On the basis of the current absorption bands, it was possible to identify the quaternary ammonium salts that are part of both agents.

Through assessing the usefulness of the proposed chromatographic approach for the identification of cotton fibers treated by selected destructive agents it can be concluded that chromatographic analyses using HPLC-DAD can be a valuable supplement for the forensic research of evidence materials. These techniques along with other pieces of research: macroscopic, microscopic and spectroscopic ones, could give a lot of information about e.g. fibers. Although the identification of reactive dyes in degraded threads is difficult to perform and not always

possible, the obtained different and characteristic chromatograms could be a useful tool differentiating the analyzed textile micro-traces.

Pieces of research performed for dyed polyester fibers were done analogically to apply to the cotton ones. The first stage was focused on developing methods of identifying nine commercially available disperse dyes by chromatographic techniques. Two HPLC-DAD methods and one UPLC-QTOF-MS method for the identification of these disperse dyes and the polyester fibers dyed by them, were developed and validated. In the next step of investigations, the different procedures for isolating dispersive dyes from single fibers were tested. The established optimal parameters for extraction were as follow: chlorobenzene as extraction solvent at 100°C for 60 minutes. The validation data and the results of the analysis of 1 mm thread confirmed the usefulness of all the proposed methods for such analyses. In the situation of overlapping signals of disperse dyes with signals from the other compounds present in the polyester, it was proposed to use methylene chloride for extraction instead of chlorobenzene.

In the next step of these investigations, the analysis of non-degraded and degraded polyester fibers using optimized and validated HPLC-DAD and UPLC-QTOF-MS methods was carried out. The samples as 5 mm, 1 mm threads of polyester and 5 mm polyester fibers were extracted in the optimized conditions and subjected to chromatographic analyses. UPLC-QTOF-MS method in comparison to HPLC-DAD ones allowed to identify the majority of disperse dyes in the tested samples. In addition, this technique is more sensitive and gives more characteristic parameters for the target dye (apart from the retention time also the characteristic [m/z] values with an accuracy of 4. decimal places, which is connected with the application of high resolution mass spectrometer as a detector).

The next stages were the macroscopic, microscopic, spectroscopic and chromatographic analyses of samples of materials and fibers of polyester non-degraded and degraded by destructive agents mentioned above. Also in this case, the greatest changes were observed during the use of Domestos and Quatovet. Domestos stiffened and slightly changed the color of the materials and fibers of polyester. The samples treated by Quatovet did not dry under the same conditions. The changes in the morphology of the fibers accentuated the research with the optical and fluorescence microscopy. These mainly concerned the samples treated by Domestos, Cidex, Sterninox and Quatovet. The IR spectra characteristic for poly (ethylene terephthalate) (PET) were obtained for both materials (non-degraded and degraded). Additional bands were observed in two cases: after degradation of Domestos and Sterinox.

Based on the usefulness of the proposed chromatographic approach (two HPLC-DAD methods and one UPLC-QTOF-MS method) for the identification of polyester fibers treated

by selected destructive agents it could be concluded that the chromatographic analysis could be a valuable supplement for the forensic research of evidence and comparative materials. These techniques with other pieces of research: macroscopic, microscopic and spectroscopic ones could give a lot of information about e.g. fibers. The identification of dispersive dyes in degraded threads is possible to conduct and the obtained different and characteristic chromatograms could be a useful in tool differentiating the micro-traces as polyester fibers.

To sum up, the analyzed textile materials and fibers undergo varying intensity of degradation. The results of performed investigations have shown that polyester fibers are more resistant to various types of destructive chemicals than the cotton ones.

Chromatographic methods for the identification of textile dyes can be a significant addition to the spectroscopic techniques commonly used in forensic examinations.

Keywords: fibers, reactive dyes, disperse dyes, forensic analysis, chromatographic methods, spectroscopic methods